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THE USE OF OSCILLOGRAPHIC POLAROGRAPHY FOR THE QUANTITATIVE DETERMINATION OF TITANIUM

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Many research workers have used a polarographic method for the determination of titanium in various objects. Zeltzer [1] got a reduction wave for titanium (IV) in weak acid media at a potential of −0.81 V (against the saturated calomel electrode). He reckoned that this wave corresponds to the process Ti (IV) + e ⟶ Ti (III). That this process was irreversible was shown by the fact that an anode oxidation curve of Ti (III) was obtained at a potential of −0.18 [2].

Acid solutions however are not very suitable for quantitative polarographic determination of titanium, since titanium salts are hydrolyzed in weak acid solutions, while in strong acid solutions (1-2 N) the titanium wave does not show up clearly and fuses into the H^+ discharge wave [2].

The use of complexing agents improves the shape of the wave, and methods have been worked out for the polarographic determination of titanium. The following materials have been used as complexing agents: tartrates, citrates [2], thiocyanates [3], oxalates [4], and Trilon B [5]. In these cases titanium (IV) forms a clearly defined wave with a half wave potential displaced to more positive values. Thus for the tartrate and citrate complex $E_{1/2}$ = −0.48 V, while $E_{1/2}$ for the complex with Trilon B = −0.43 V (saturated calomel electrode) at a pH of 4.6. The titanium complexes are reversibly reduced, as one of us showed in the case of the complex with Trilon B [5]. The process can be schematically represented by the following reaction: Ti(IV) + e ⇌ Ti(III).

Zanko and coworkers developed a polarographic method for the determination of titanium in bauxite, kaolin, slags [6], casts, and steels [7], in which they used a 14% solution of tartaric acid in 0.1 N sulfuric acid as complexing agent. Using a calculating method they got relative errors of 4-5% for a titanium content of 0.4-1%. They did not study the effect of vanadium on the titanium wave.

Calculating methods [8] usually give errors considerably in excess of 4-5%, and the nature and concentration of other elements accompanying the titanium have a considerable effect on the value of the real diffusion coefficient of titanium.

1 N H_2SO_4 saturated with sodium oxalate and containing 8% urea as a maximum suppressor [4] was used for determination of titanium in clays. According to the author iron does not interfere, but the effect of vanadium was not studied.

A study of the value of $E^{1/2}$ for this complex showed that $E^{1/2}$ is independent of the concentrations of titanium and iron [9].

The preparation of a saturated solution of sodium oxalate in 1 N H_2SO_4 with a concentration of 8% urea is, however, impossible. In addition we could not establish that urea has a positive effect on the influence of iron on the titanium diffusion current.

Our aims were:

1. To develop a polarographic or oscillographic method of determining titanium in the presence of a number of elements: iron, vanadium, chromium, nickel, etc.

2. To elucidate the mechanism of the reduction of titanium (IV) complexes and to explain the stability of the tartrate, citrate, and oxalate complexes of Ti in 1-2 N sulfuric acid.

We accordingly studied the behavior of titanium (IV) complexes on the dropping mercury cathode in 1 N sulfuric acid using the ordinary and oscillographic polarographs.

EXPERIMENTAL

Apparatus. Measurements were made on a Heyrovsky photographic recording polarograph using a polarograph with a sensitivity of $2.21 \cdot 10^{-9}$ A/mm, and an oscillographic polarograph constructed by one of us. This instrument has been described previously [10].

The frequency of the saw-toothed vibrations of the generator was measured with a counter which registered the number of sweeps per unit time. The saw-toothed voltage applied to the cell was measured either with a tube voltmeter or potentiometrically. The cell consisting of a dropping mercury cathode and a saturated calomel electrode was well screened from interference. The drop time of the cathode (t) varied within the limits 6-7.3 seconds during oscillographic measurements, while the characteristics of the capillary used for polarographic determinations were as follows: $m^{2/3} t^{1/6} = 1.434$ $mg^{2/3} \cdot sec.^{-1/2}$ in 1 N solution of KCl – 0.05 N HCl at –0.8 V.

All the potentials quoted are referred to the saturated calomel electrode.

Solutions and Reagents. a) The stock solution of titanium sulfate was prepared by a three-fold treatment of an aliquot of potassium fluorotitanate with sulfuric acid, the mixture being heated to evolution of sulfuric fumes. The cooled solution was diluted to a known volume and the titanium content determined gravimetrically as TiO_2 after precipitation with ammonia. After dilution with 1 N H_2SO_4, 1 liter contained 0.2700 g Ti. b) Sodium oxalate, tartaric and citric acids were chemically pure or analytical grade chemicals; the hydrazine was recrystallized from water. c) Solutions of ammonium vanadate and of salts of Fe(III), Cr(III), Ni and Mo(VI) were prepared by the usual methods and their concentrations established chemically.

I. The Polarographic Wave of Titanium in the Presence of Iron and Vanadium

Titanium gives a clearly defined wave with $E_{1/2} = -0.3$ V in 1 N H_2SO_4 saturated with sodium oxalate. There is a straight line relation between the diffusion current and Ti concentration. The mean diffusion constant of the current is K = 2.0. In order to study the effect of iron and vanadium on the Ti(IV) diffusion current, various amounts of iron and vanadium (in 1 N H_2SO_4 saturated with sodium oxalate) were added to the test solution containing the same amount of titanium as in the solutions in which titanium was used on its own.

Fig. 1 shows that iron lowers the Ti(IV) wave by 40% for an iron concentration twice that of titanium.

When the Fe(III) concentration is four times that of titanium, the titanium polarographic wave is distorted and a maximum is formed on the polarogram (Curve 3, Fig. 1).

When the concentration of Ti(IV) and V(V) are roughly the same, the latter leads to an increase of 50% in the titanium wave as compared with the value of the Ti(IV) limiting current in the absence of vanadium. The origin of the titanium wave is not clearly shown (compare Curves 1 and 4, Fig. 1).

When the vanadium concentration is four times that of titanium, a maximum appears on the polarogram and the limiting current decreases with increasing applied potential, while the origin of the wave becomes indistinct as well (Curve 5, Fig. 1).

Ordinary polarography, therefore, cannot be used for quantitative determination of titanium in the presence of iron and vanadium without preliminary removal of the latter.

II. Oscillographic Curves of Titanium in Acid Media.

An oscillogram was taken of a $4.227 \cdot 10^{-4}$ M solution of Ti(IV) in 1 N H_2SO_4 (Fig. 2). The solution was electrolyzed at an amplitude of −1.4 V for the saw-toothed voltage in the absence of atmospheric oxygen. The oscillogram was recorded for one mercury drop at its maximum cross-section (at the point when the drop is falling off). Voltage applied to the polarographic cell is plotted along the abscissa while the current flowing through the cell is plotted along the ordinate. The oscillogram (Fig. 2) shows a curve rising sharply from the left, which is caused by the current from the charged mercury surface, the shape being determined by the impulse applied to the cell. The maximum value of the capacity current appears at an amplitude of $E\sim = -0.5$ V of the saw-toothed voltage. This is followed by a sharp fall in the curve to $E\sim = -0.77$ V. At a value of −0.81 V there is an increase in the current as the result of reduction of Ti(IV) ions. The maximum current I_{max} is −1.61 μA, at $E\sim = -1.4$ V, a discharge of hydrogen ions begins as a consequence of which the current increases rapidly.

Complexing agents (oxalic, tartaric, and citric acids) were added to the solution to improve the titanium oscillographic curve. In Fig. 3 an oscillogram is shown in which 1 N H_2SO_4 saturated with sodium oxalate and containing $4.277 \cdot 10^{-4}$ M titanium was used. This oscillogram also represents the process occurring on one mercury drop at maximum size. The surge at the beginning of the oscillographic curve corresponds to the capacity current. The maximum value of the capacity current is attained at a potential of −0.16 V, the current then remains practically constant up to a voltage of −0.3 V. At $E\sim = -0.3$ V the current increases rapidly as a result of the reduction of the Ti(IV) complex. The diffusion of Ti(IV) ions from the body of the solution to the layer near the electrode starts off from this point.

Starting from the reduction potential of quadrivalent titanium the current increases as a result of an increase in the concentration gradient in the layer adjacent to the electrode. The maximum value of current is reached at −0.5 V. After $E\sim = -0.5$ V there is a decrease in current strength; this is determined by a decrease in concentration gradient in the effective diffusion layer. Under the conditions which hold during oscillographic polarography, therefore, we get concentration polarization and I_{max} is a diffusion current for which $\left(\frac{\partial e}{\partial r}\right)_{r=0}$ has a maximum value. The value of the maximum titanium current for a $4.227 \cdot 10^{-4}$ M solution of titanium in 1 N H_2SO_4 saturated with sodium oxalate is 9.64 μA.

Figs. 2 and 3 were recorded for the same frequency of generator sweeps.

The oscillogram in Figs. 2 and 3 show that I_{max} of the Ti(IV) oxalate complex in 1 N H_2SO_4 is 6 times greater than I_{max} for hydrated Ti(IV) in 1 N H_2SO_4. The reduction potential of the Ti(IV) oxalate complex in 1 N H_2SO_4 is displaced by 0.51V to more positive values of E ~. This fact indicates that the Ti(IV) oxalate complex is stable in 1 N H_2SO_4. The Ti(IV) citrate and tartrate complexes,as our experiments showed,are destroyed at such low pH's; while E ~ of Ti(IV) in these media is −0.81 V and the value of the maximum titanium current is the same as in the absence of complexing agents.

It is possible to get clearly defined Ti(IV) waves in 1 N H_2SO_4 by the use of oscillographic polarography (Fig. 2),while this is impossible on an ordinary polarograph since the Ti wave fuses into the H^+ discharge wave (Fig. 4). In order to explain the reason for the large difference in the value of the maximum current of Ti(IV) in 1 N H_2SO_4 saturated with sodium oxalate and in the absence of oxalate,a number of measurements were made of the titanium diffusion coefficient in these media using diffraction methods. It was found that the diffusion coefficient of the Ti(IV) oxalate complex in 1 N H_2SO_4 is $7.22 \cdot 10^{-6}$ cm^2/sec, while D Ti(IV) in 1 N H_2SO_4 is $2.2 \cdot 10^{-6}$ cm^2/sec. Thus the diffusion coefficient of Ti(IV) in 1 N H_2SO_4 is approximately 3.3 times less than that of D for the Ti(IV) oxalate complex in 1 N H_2SO_4.

Titanium as the cation is known to be reduced in 1 N H_2SO_4. Since both the nature and concentration of an indifferent electrolyte affects the value of the cationic diffusion coefficient, then sulfuric acid as an electrolyte with 1,2 valencies significantly decreases the value of D of Ti(IV). The titanium diffusion current is accordingly small.

It is also known that [8] the value of the anionic diffusion coefficient increases on addition of an indifferent electrolyte,as in the case of the iodate ion. Probably sulfuric acid and excess $Na_2C_2O_4 \cdot 2H_2O$ has such an effect on the value of D for the Ti(IV) oxalate complex, increasing it to $7.22 \cdot 10^{-6}$ cm^2/sec.

As a consequence, the increase in the titanium diffusion coefficient in 1 N H_2SO_4 saturated with $Na_2C_2O_4 \cdot 2H_2O$,and the displacement of the reduction potential of the Ti(IV) complex to more positive potentials, indicate that at E ~ = −0.3 V it is the anion of quadrivalent titanium that is reduced. As a result the maximum current in 1 NH_2SO_4 saturated with sodium oxalate is greater than I_{max} for Ti(IV) in 1 N H_2SO_4 in the absence of sodium oxalate, for equal concentrations of titanium in both cases.

The time taken by the value of the Ti concentration gradient in 1 N H_2SO_4 saturated with $Na_2C_2O_4 \cdot 2H_2O$ to reach its maximum is 21 milliseconds.

In the case of the reduction of the quadrivalent titanium cation in H_2SO_4 of the same titanium concentration,but in the absence of a complexing agent the maximum value of $\left(\frac{\partial c}{\partial r}\right)_{r=0}$ of Ti(IV) is reached in 10 milliseconds.

III. The Effect of Rate of Potential Change on the Value of the Maximum Current of the Reduced Ti(IV) Oxalate Complex.

The effect of the rate of potential change on the value of the maximum current of the Ti(IV) oxalate complex in 1 N H_2SO_4 was studied.

The rate at which the potential applied to the cell changes (α) depends both on the frequency of the generator sweeps (ν) and on the amplitude of the saw-toothed voltage (E ~). The product of these two factors gives the rate of change of the saw-toothed voltage applied to the electrolytic cell. The following values were obtained for the maximum current (Table 1) for a $2.818 \cdot 10^{-4}$ M solution of Ti(IV) in 1 N H_2SO_4 saturated with sodium oxalate (in the absence of oxygen).

TABLE 1

Effect of the Rate of Change of Potential on the Value of the Maximum Reduction Current of Ti(IV). $2.818 \cdot 10^{-4}$ M Ti(IV) in 1 N H_2SO_4 saturated with $Na_2C_2O_4 \cdot 2H_2O$; m = 0.88 mg/sec; t = 7.1 sec, E ~ = 0.6 V (with respect to saturated calomel electrode); h = 440 mm; R = 1500 Ω

Frequency of the saw-tooth voltage generator, sweeps/sec (ν)	Rate of change of potential in V (α)	$\alpha^{1/2}$	Maximum current in μ A (found)
3.75	2.25	1.50	2.65
4.50	2.70	1.64	2.76
5.02	3.01	1.74	2.87
6.00	3.60	1.89	3.31
7.80	4.68	2.16	4.08
9.00	5.40	2.32	4.63
11.00	6.60	2.57	5.07
12.30	7.38	2.77	6.17
13.10	7.86	2.80	6.40
13.60	8.16	2.85	6.51
14.30	8.58	2.93	6.62

TABLE 2

Maximum Current Values for Various Ti(IV) Concentrations in 1 N H_2SO_4 Saturated with $Na_2C_2O_4 \cdot 2H_2O$; m = 0.88 mg/sec; t = 7.1 sec; ν = 12 sweeps/sec; α = 7.2 V/sec; h = 440 mm

μg Ti/ml	Concentration of Ti in mol/liter	Maximum current in μ A
27.00	$5.636 \cdot 10^{-4}$	11.91
20.25	$4.227 \cdot 10^{-4}$	8.93
13.50	$2.818 \cdot 10^{-4}$	5.95
6.75	$1.409 \cdot 10^{-4}$	2.98
2.70	$5.636 \cdot 10^{-5}$	1.20
1.35	$2.818 \cdot 10^{-5}$	0.60
0.67	$1.398 \cdot 10^{-5}$	0.30

The results given in Table 1 show that with increasing rate of change of the saw-tooth potential, the titanium maximum current increases. It is essential, therefore, when carrying out quantitative Ti determinations to work at a strictly constant rate of change of potential.

IV. Relation between the Titanium Maximum Current and Titanium Concentration.

Experiments were made in order to check the linear relation between the value of the maximum current of Ti(IV) and its concentration. To 1 N H_2SO_4 saturated with sodium oxalate was added various amounts of titanium, and the solution electrolyzed in the absence of atmospheric oxygen. Results are given in Table 2.

The results given in Table 2 indicate a linear relation between diffusion current and titanium concentration.

The sensitivity of the oscillographic method is considerably higher than that of the ordinary polarographic method. Curves 1 and 2, Fig. 5 correspond to a solution containing 1.0 and 0.4 μ g Ti/ml respectively in 1 N H_2SO_4 saturated with sodium oxalate. Curves 1 and 2 were taken for one mercury drop at its maximum size while Curve 3 was obtained on an ordinary polarograph in a solution containing 5 μ g Ti/ml in the same supporting electrolyte.

Despite the fact that the Ti concentration in Curve 2 is 12.5 times less than in Curve 3, the oscillogram is still clearly defined and can be used for quantitative determination of Ti. It is impossible to determine such a small amount on the ordinary polarograph. The high sensitivity of the oscillographic method as compared with the ordinary polarograph method is the result of the considerable difference in the rate of increase of the voltage in the impulse applied to the electrolytic cell.

V. Effect of Iron, Vanadium, Molybdenum, Chromium, and Nickel on the Value of the Maximum Ti Current

a) Effect of Iron and Vanadium.

Experiments in which solutions of vanadium and iron salts were added to the test titanium solution were made in order to establish the effect of iron and vanadium on I_{max} for Ti(IV) in 1 N H_2SO_4 saturated with sodium oxalate. The solutions were electrolyzed in the absence of atmospheric oxygen (Table 3).

TABLE 3

Effect of Various Concentrations of Iron and Vanadium on the Value of the Ti(IV) Maximum Current. m = 0.88 mg/sec; t = 7.1 sec; ν = 12 sweeps/sec; α = 7.2 V/sec; h = 440 mm

Expt. No.	Amount of metal taken in μg/ml			Maximum value of the Ti current in μA
	Ti(IV)	Fe(III)	V(V)	
1	10	–	–	4.41
2	10	25	–	4.41
3	10	50	–	4.41
4	10	100	–	4.38
5	10	250	–	4.39
6	10	1500	–	2.28
7	20	100	–	8.80
8	20	200	–	8.82
9	30	300	–	13.25
10	10	–	25	4.40
11	10	–	50	4.45
12	10	–	75	5.10
13	10	–	100	5.41
14	30	–	150	13.28
15	40	–	200	17.69
16	5	250	100	2.28
17	10	250	100	4.43
18	20	250	100	8.80
19	30	250	100	13.21
20	5	500	100	2.18
21	10	500	100	4.36
22	20	500	100	8.69
23	30	500	100	13.12

The results given in Table 3 show that trivalent iron does not affect the maximum diffusion current of Ti up to a ratio of iron to titanium of 25:1 (Experiments 1-5).

For higher ratios of Fe(III):Ti(IV) there is a decrease in the I_{max} of titanium (Experiment 6). Vanadium does not affect the maximum current of Ti until a ratio of V:Ti of 5:1 is reached, and the oscillographic wave of titanium begins to increase when the amount of vanadium in solution becomes 6 or more times that of the Ti(IV) concentration.

When both iron and vanadium are present simultaneously, their effect on the Ti current is not so pronounced as when they are present in the Ti solution separately. E.g., at a ratio of Fe:Ti of 100:1 and of V:Ti of 20:1, there is practically no effect on the value of I_{max} for titanium (Experiment 20, Table 3).

The linear relation between titanium concentration and the value of I_{max} within the titanium concentration range of 5-30 μg/ml is maintained even for a concentration of Fe(III) of 500 μg/ml and of V(V) of 100 μg/ml. Nevertheless for iron and vanadium contents which are respectively 100 and 20 times greater than the titanium concentration, these metals begin to affect the Ti(IV) oscillographic wave.

Fig. 6, e.g., represents the oscillograms obtained in 1 N H_2SO_4 saturated with sodium oxalate and containing various amounts of titanium, while the iron and vanadium concentrations are maintained constant.

Each curve represents the process which occurs on the mercury drop at its

maximum size. In all the test solutions Fe(III) = 500 μg/ml and V(V) = 75 μg/ml. Curves 1-4, Fig. 6 show that the titanium oscillographic curves are clearly defined and that the linear relation between the maximum current of Ti(IV) and Ti concentration is maintained with great accuracy despite the fact that the amounts of vanadium and iron are several times greater than that of titanium in the test solution.

A comparison of the oscillograms in Fig. 6 with the polarograms of Fig. 1 obtained with an ordinary polarograph shows that titanium can be determined in the presence of considerable amounts of iron and vanadium without a preliminary separation of the latter when an oscillographic method is used. This is impossible on an ordinary polarograph; in the latter case, Fe(III) and V(V) must be separated from titanium beforehand (Curves 1-4, Fig. 6, and Curves 2-4, Fig. 1).

b) Effect of Molybdenum, Chromium, and Nickel on I_{max} Ti.

Solutions of Ti(IV), molybdenum, chromium, and nickel in 1 N H_2SO_4 saturated with sodium oxalate were used for studying the effect of these elements on the maximum diffusion current of Ti. Results are given in Table 4. Solutions were electrolyzed in the absence of atmospheric oxygen.

The results given in Table 4 show that molybdenum has a considerable effect on the value of I_{max} for titanium. Even for a ratio of Mo(VI)/Ti(IV) = 0.6, the value of I_{max} for Ti(IV) increases by 15.7% (Experiments 1 and 2). For approximately equal amounts of Ti(IV) and Mo(VI) the latter increases the oscillographic wave of Ti(IV) by almost 30% (Experiment 3). The presence of iron and vanadium in a test solution containing Ti(IV) and molybdenum does not diminish the effect of Mo(VI) on the value of I_{max} for titanium. Chromium (III) and nickel (II) have practically no effect on I_{max} for titanium. In all cases the oscillographic wave of Ti(IV) is clearly expressed. Although molybdenum has this appreciable effect on the value of I_{max} for titanium, titanium can nevertheless be still determined in the presence of molybdenum if a calibration curve is taken for solutions containing Ti(IV) with the same amount of molybdenum in them as in the test sample.

TABLE 4

The Effect of Molybdenum, Chromium, and Nickel on the Oscillographic Wave of Titanium

m = 0.88 mg/sec; t = 7.1 sec; ν = 8.8 sweeps/sec; E ~ = −0.97 V; α = 8.53 V/sec; h = 440 mm

Expt. No.	Amount of metal taken in μg/ml						Maximum Ti(IV) current in μA
	Ti(IV)	Mo(III)	Fe(III)	Cr(III)	V(V)	Ni(II)	
1	60.73	–	–	–	–	–	29.78
2	60.73	36.5	–	–	–	–	34.45
3	60.73	73.0	–	–	–	–	38.75
4	13.50	–	–	–	–	–	6.62
5	13.50	–	–	40.5	–	–	6.59
6	13.50	–	–	81.0	–	–	6.66
7	13.50	–	–	150	–	–	6.52
8	13.50	–	–	–	–	54	6.64
9	60.73	36.5	300	–	60	–	33.15

VI. An Oscillographic Method of Determining Titanium in Steels

Methods of determining titanium in steels containing vanadium, iron, cobalt, nickel, chromium, and copper usually take a long time and necessitate removal of some of these metals. The use of oscillographic polarography in this instance is therefore of interest.

A normal analysis takes 4-6 hours.

An oscillographic analysis takes 20 minutes after dissolving the sample. The following procedure was adopted:

0.5-2 g of steel turnings was dissolved in H_2SO_4, and HNO_3 added [11]. When the steel had dissolved, the acidity of the solution varied from 2-5 N with respect to H_2SO_4.

An amount of test solution was transferred to a 50 ml beaker such that the normality of the solution after dilution was exactly 1 N. The solution was then boiled with hydrazine sulfate to reduce any iron. When the solution had cooled, it was saturated with sodium oxalate and diluted to exactly 5 or 10 ml. The solution was then transferred to the electrolytic cell, hydrogen bubbled through to remove oxygen, and then electrolyzed. Having obtained the oscillogram, the value of the maximum current of titanium was determined, and the amount of titanium determined by the method of additions.

When the second oscillogram had been recorded, the initial concentration of Ti(IV) was calculated from the increase in diffusion current caused by the addition of a known amount of titanium. Determination of the maximum Ti(IV) current was done visually. Results for steel analyses are given in Table 5; results are also given for Ti content as determined by other methods in the Stalin Steel Institute.

TABLE 5

Determination of Titanium in Steels by Means of Various Methods

Sample No.	1	2	3	4	5
Composition of steel in %					
Carbon	0.58	1.05	1.02	0.15	0.14
Silicon	0.69	–	–	0.36	0.52
Sulfur	0.04	–	–	0.012	0.013
Phosphorus	0.026	–	–	0.022	0.031
Chromium	17.50	8.0	5.74	1.68	25.79
Nickel	8.58	–	0.13	0.21	0.31
Copper	0.24	–	0.06	–	0.34
Manganese	–	–	0.32	1.58	0.26
Aluminum	–	–	–	–	5.71
Cobalt	–	10.2	5.94	–	–
Vanadium	–	2.06	0.1	–	–
Results of determination of Ti in %					
Cupferron colorimetric method (Steel Institute)	0.40	–	0.69	0.037	0.031
Gravimetric method (Steel Institute)[1]	–	2.28	–	–	–
Oscillographic method	0.41	2.36	0.68	0.030	0.027
Difference in %	+2.5	+3.5	−1.45	−19.0	−13.0

[1]) Vanadium was separated from titanium by fusion with Na_2CO_3 and boiling with NaOH.

The results given in Table 5 show that those obtained by the oscillographic method are in good agreement with those of colorimetric and gravimetric determinations (with the exception of Samples 4 and 5). Since for the cupferron-colorimetric method of analyzing samples containing less than 0.05% titanium, a deviation between duplicates of ±20% was tolerated [11], then the agreement between the results of oscillographic and colorimetric methods for Samples 4 and 5 can be regarded as satisfactory. More accurate determinations

of titanium in steel can be made if the oscillograms are photographically recorded.

A number of oscillograms obtained for Ti(IV) in steels are adduced in Fig. 7 as examples.

Curve 1 corresponds to Sample No. 1, Curve 2 to Sample No. 3, while Curve 3 corresponds to Sample No. 3 after 0.5 ml of a standard solution of titanium has been added to the electrolytic cell. Oscillograms 1, 2, and 3 were recorded for one drop of mercury at its maximum size. Curve 4 corresponds to Sample No. 4 and was recorded during the growth of one mercury drop.

Oscillographic waves for titanium which appeared at a potential of −0.3 V are clearly defined and can be measured accurately.

The authors wish to thank Prof. A. M. Dymov for his gifts of steel samples.

SUMMARY

1. The reduction of titanium in acid media on a dropping mercury cathode has been studied by means of oscillographic polarography.

It has been established that titanium in the form of a cation is reduced in 1 N H_2SO_4 at −0.81 V (saturated calomel electrode). In a solution of sulfuric acid of the same concentration but saturated with sodium oxalate, it is the anion of the Ti(IV) oxalate that is reduced.

2. Investigation of the effect of tartrate and citrate on the titanium wave in 1 N H_2SO_4 showed that at this low pH both the tartrate and citrate complexes of Ti(IV) break down.

3. It has been shown that it is best to detemine titanium in acid media saturated with sodium oxalate.

4. It has been established that there is a linear relation between the titanium diffusion curve on the oscillograms and the titanium concentration of the solution.

5. The effect of iron, vanadium, chromium, nickel, and molybdenum on the maximum current of titanium has been studied. It has been shown that if the amount of iron is 100 and that of vanadium 20 times respectively, greater than the Ti(IV) concentration, then there is no effect on the value of I_{max} for titanium. Chromium and nickel also show no effect on I_{max} for titanium. Molybdenum, however, has a considerable effect on I_{max} for titanium and increases the current.

6. It has been established that normal polarography does not permit a quantitative determination of titanium in the presence of vanadium and iron without a preliminary separation of Ti(IV). The possibility has been demonstrated of determining titanium in steels without preliminary separation of vanadium and iron.

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The Use of Oscillographic Polarography for the Quantitative Determination of Titanium – p. 283.

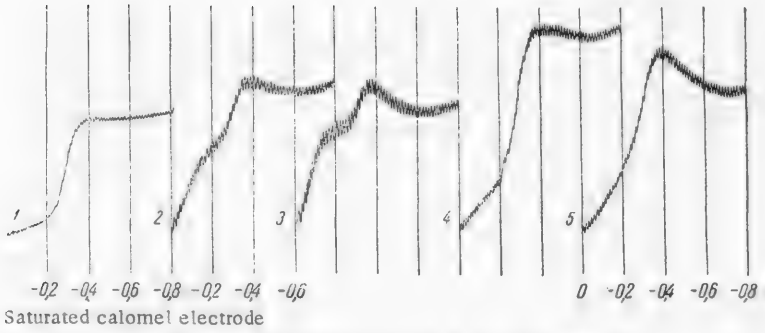


Fig. 1. Polarograms for titanium in presence of iron and vanadium.

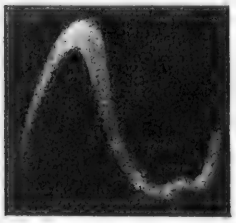


Fig. 2. Oscillographic curve for titanium in 1 N H_2SO_4

Fig. 3. Oscillographic curve for titanium in 1 N H_2SO_4 saturated with sodium oxalate.

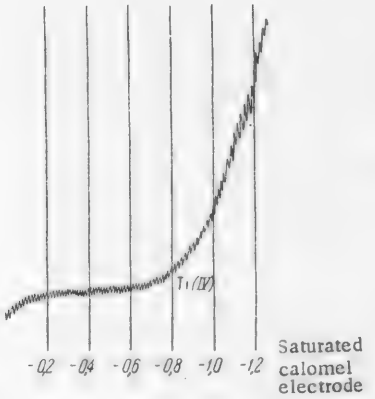
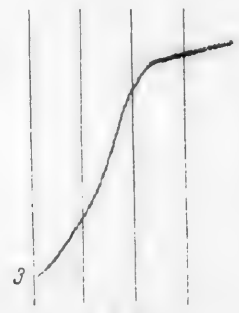


Fig. 4. Polarogram of titanium in 1 N H_2SO_4.



a *б*

Fig. 5. Oscillographic curves of titanium (a) and a polarogram of Ti(IV) (b) in 1 N H_2SO_4 saturated with sodium oxalate.

Fig. 6. Oscillographic curves for titanium in the presence of iron and vanadium.

Fig. 7. Oscillographic curves for titanium contained in steels.

Spectroscopic Determination of Strontium and Lithium in Natural Waters – p. 295.

Fig. 1. Atomizer for spraying solution into the arc flame.

SPECTROSCOPIC DETERMINATION OF STRONTIUM AND LITHIUM IN NATURAL WATERS

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The amounts of lithium and strontium in natural waters has interested research workers for a long time. A number of investigations has been devoted to the determination of lithium and strontium in sea water. On the basis of these results it has been accepted that the amount of lithium in sea water is $1.2 \cdot 10^{-5}$%; the amount of strontium is somewhat greater; according to a number of determinations including those carried out by A. P. Vinogradov and T. F. Borovik-Romanova, it is equal to $1 \cdot 10^{-3}$% [1]. There is considerably less strontium in river water; according to results obtained by one of the authors of the present article for a number of rivers in Western Trans-Baikal, it varies from $6 \cdot 10^{-6}$ to $7 \cdot 10^{-5}$%. The amount of lithium in river water according to V. I. Vernadsky's results ranges from $3.2 \cdot 10^{-6}$ to $1 \cdot 10^{-5}$% [2]. A. P. Vinogradov has pointed out more than once that for a better understanding of the origin of rocks and minerals and the method of migration of elements, a knowledge of the ratio between pairs of elements similar to each other in physico-chemical properties such as Ca/Sr, K/Rb, etc. is of considerable importance.

It has been found that the ratio of Ca/Sr is ca. 30 for sea water, while for river water, Ca/Sr is ca. 150 [3].

In the work described in this article determinations were made of strontium and lithium in a number of natural waters, mainly of chlorine, sodium and magnesium-containing waters (ca. 200 samples) of various origins. It was found that the amount of strontium in the waters tested varied from $1 \cdot 10^{-5}$ to $1 \cdot 10^{-3}$%, while the amount of lithium varied from $1 \cdot 10^{-7}$ to $1 \cdot 10^{-4}$%. The value of the ratio between calcium and strontium in the waters tested enabled us to assess whether the water was of sea or continental origin.

Method for the Determination of Strontium and Lithium in Natural Waters

In 1939-1940 S. A. Borovik and T. F. Borovik-Romanova worked out spectrographic methods for determining small amounts of strontium in solution by means of a condensed spark [4], and also by means of a D.C. arc. In the latter instance calcium was isolated from the test waters and its strontium content determined; lithium was determined by means of a flame. In 1950 S. A. Borovik and T. F. Borovik-Romanova used an H. F. spark for determinations of strontium in solution [5], and also an A.C. arc of the Sventitsky type in which a specially constructed atomizer was used [6]. By means of the condensed spark method it

was possible to determine $5 \cdot 10^{-4}$% Sr, but the sensitivity of the spark discharge method for lithium was low – $1 \cdot 10^{-3}$%; such sensitivity is not high enough for solving the problems we are interested in at present. The same is true of the H.P. spark. Since an activated A.C. arc of the Sventitsky type showed a sufficiently high sensitivity for determination of strontium and lithium, we chose this as an excitation source for simultaneous determinations of lithium and strontium in water.

We finally chose the following operating conditions: the excitation source was an A.C. arc operating at 120 V, with a current strength of ca. 2.0 A. The solution was sprayed into the arc flame by means of an atomizer (Fig. 1, see plate, page 293.) [5].

The atomizer consists of a quartz vessel 2 cm in diameter and 1 cm deep.

The vessel has a tubular nozzle, the top end of which is a ground glass cone. A carbon electrode 1.5 cm long is fitted into this cone, the upper end of the electrode is ground to a blunt wedge along which a narrow vertical groove is made, 3 mm deep, and in addition a channel 0.8 cm in diameter is drilled along the carbon axis. The channel terminates in side tubes on both sides of the carbon electrode near the bottom of the vessel; the channel serves to lift the liquid by capillary action to the upper end of the carbon electrode and ensures a continuous supply of solution to the arc flame.

The amount of liquid fed into the vessel is 1.5 cm^3.

A copper spiral is used as a current lead-in. The spiral, which at the same time is a spring, presses the contact, which is a copper wire with a platinum tip, to the lower end of the electrode.

The vessel is clamped in the arc stand.

The upper electrode is a carbon rod 6 mm in diameter, sharpened to a wedge, but without a groove.

The electrodes are mounted so that the edges of the wedges are arranged along the optical axis.

A three-prism glass spectrograph – the ISP-51 – with a camera of F = 270 mm, was used.

A two-lens system was used for illumination; the opening in the movable diaphragm was 3.2 mm, the arc length – 4 mm, the spectrograph slit – 0.02 mm[1)], exposure time – 2 minutes. The arc was operated for 1 minute while the spectrograph slit was closed in order to get stable conditions for feeding the solution to the arc. The test waters were similar in composition to the dry residue, but differed in concentration, which

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[1)] It is recommended that a two-stage clearing agent be fitted in front of the spectrograph slit.

was first adjusted by diluting or evaporating so that the dry residue in each case was ca. 0.015 g/cc. Standard solutions were prepared near in composition and concentration to the test solution; they contained 1.7% NaCl, 0.45% $MgCl_2 \cdot 6H_2O$, and 0.95% $CaCl_2 \cdot 6H_2O$, respective amounts of $SrCl_2$ and LiCl were added to these solutions. The final standards contained the amounts of strontium and lithium adduced in Table 1.

The solutions of the main elements contained insignificant amounts of strontium, the amount of strontium actually present was determined by the method of addition [7], and was taken into account with the amount of strontium added to the standard solution.

A solution of cesium nitrate containing 1% Cs was added in the ratio of 2:1 to the standard and test samples; cesium was used as the reference element.

For analysis the 4607.331 A line was used for strontium and the 6707.844 A line for lithium; the lines of the reference element were 4593.103 A and 6723.279 A.

The wave lengths and excitation potentials of the lines used are adduced in Table 2.

TABLE 1

No. of standard	Sr content, in %	Li content, in %
0	$8.1 \cdot 10^{-3}$	$6.6 \cdot 10^{-4}$
I	$2.7 \cdot 10^{-3}$	$2.2 \cdot 10^{-4}$
II	$9.0 \cdot 10^{-4}$	$7.3 \cdot 10^{-5}$
III	$3.0 \cdot 10^{-4}$	$2.4 \cdot 10^{-5}$
IV	$1.0 \cdot 10^{-4}$	$8.0 \cdot 10^{-6}$
V	$3.4 \cdot 10^{-5}$	$2.7 \cdot 10^{-6}$

TABLE 2

Wave length of test element (Å)	Excitation potential, in eV	Wave length of reference element (Å)	Excitation potential, in eV
Sr 4607.33	2.69	Cs 4593.103	2.70
Li 6707.844	1.80	Cs 6723.278	–

Panchromatic plates of sensitivity 1200 H. and D. were used for detection of lithium; the strontium line, however, was too intense when these plates were used. A device suggested by S. A. Borovik was accordingly adopted; the photographic plate was made in two parts: one ortho (or reproduction) and the other panchromatic. The panchromatic part was fixed in the part of the cell where the part of the spectrum from 5000-6730 A was incident, while the other part was located near the outer edge of the cell, where the 4250-5000 A part was incident. Samples and standards were photographed on the same plate, twice in each case. Using the ISP-51 spectrograph with an F = 270 mm camera, it was possible to get spectrograms of 23 samples and 4 standards on one plate. The blackenings of the lines indicated above for strontium, lithium and cesium were measured on a microphotometer in order to determine the strontium and lithium contents; the respective concentrations were determined from calibration curves plotted along the coordinates of ΔS, log C. Fig. 2 shows that the graph is linear for strontium within the limits $2.2 \cdot 10^{-4}$ to $6 \cdot 10^{-3}$, for lithium from $1.0 \cdot 10^{-5}$ to $5.0 \cdot 10^{-4}$%. The relative experimental error (mean arithmetic) was found for replicates to be $\pm$6-8%. Results of replicates for lithium are given in Table 3.

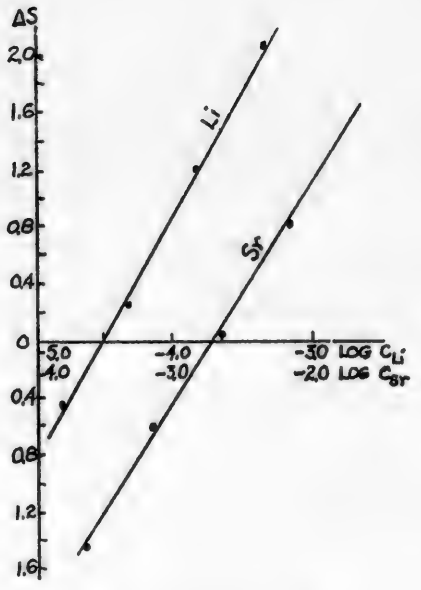

Fig. 2. Calibration curves for determination of Sr and Li in natural water.

TABLE 3[1])

Expt. No.	Amount of Li added, in %	Amount of Li found, in %	Relative error, in %
1	$2.7\cdot10^{-5}$	$2.7\cdot10^{-5}$	0
2	$2.7\cdot10^{-5}$	$2.6\cdot10^{-5}$	−3.7
3	$2.7\cdot10^{-5}$	$2.6\cdot10^{-5}$	−3.7
4	$2.7\cdot10^{-5}$	$2.9\cdot10^{-5}$	+7.4
5	$2.7\cdot10^{-5}$	$2.4\cdot10^{-5}$	−12.5
6	$2.7\cdot10^{-5}$	$2.8\cdot10^{-5}$	+3.7
7	$2.7\cdot10^{-5}$	$2.9\cdot10^{-5}$	+7.4
8	$2.7\cdot10^{-5}$	$2.6\cdot10^{-5}$	−3.7
9	$2.7\cdot10^{-5}$	$3.1\cdot10^{-5}$	+14.8

Table 4 contains the results obtained on one plate for the lithium and strontium content of some test waters. Each determination is the mean of duplicates.

These results show that the method worked out for determination of strontium and lithium in water is highly sensitive and is reasonably accurate.

TABLE 4

Sample No.	Concentration of Li in two parallel determinations, in %		Mean Li concentration, in %	Concentration of Sr in two parallel determinations, in %		Mean Sr concentration, in %
108	$1.26\cdot10^{-5}$	$1.22\cdot10^{-5}$	$1.24\cdot10^{-5}$	$6.6\cdot10^{-3}$	$5.0\cdot10^{-3}$	$5.8\cdot10^{-3}$
110	$0.9\cdot10^{-5}$	$0.7\cdot10^{-5}$	$0.8\cdot10^{-5}$	$7.5\cdot10^{-3}$	$8.0\cdot10^{-3}$	$7.8\cdot10^{-3}$
120	$0.8\cdot10^{-5}$	$0.7\cdot10^{-5}$	$0.75\cdot10^{-5}$	$9.8\cdot10^{-3}$	$9.8\cdot10^{-3}$	$9.8\cdot10^{-3}$
122	$4.2\cdot10^{-5}$	$4.9\cdot10^{-5}$	$4.6\cdot10^{-5}$	$4.0\cdot10^{-3}$	$4.0\cdot10^{-3}$	$4.0\cdot10^{-3}$
123	$1.6\cdot10^{-3}$	$1.9\cdot10^{-3}$	$1.7\cdot10^{-3}$	$14\cdot10^{-2}$	$16\cdot10^{-2}$	$15\cdot10^{-2}$
125	$7.4\cdot10^{-4}$	$7.0\cdot10^{-4}$	$7.2\cdot10^{-4}$	$4.2\cdot10^{-2}$	$3.6\cdot10^{-2}$	$3.9\ 10^{-2}$
126	$1.7\cdot10^{-4}$	$1.7\cdot10^{-4}$	$1.7\cdot10^{-4}$	$1.2\cdot10^{-2}$	$1.5\cdot10^{-2}$	$1.35\cdot10^{-2}$
145	$1.3\cdot10^{-4}$	$1.5\cdot10^{-4}$	$1.4\cdot10^{-4}$	$6.0\cdot10^{-3}$	$7.0\cdot10^{-3}$	$6.5\cdot10^{-3}$
150	$6.0\cdot10^{-5}$	$6.4\cdot10^{-5}$	$6.2\cdot10^{-5}$	$7.4\cdot10^{-3}$	$9.2\cdot10^{-3}$	$8.3\cdot10^{-3}$
158	$1.2\cdot10^{-5}$	$0.9\cdot10^{-5}$	$1.0\cdot10^{-5}$	$0.5\cdot10^{-3}$	$0.42\cdot10^{-3}$	$0.46\cdot10^{-3}$
171	$8.2\cdot10^{-4}$	$8.0\cdot10^{-4}$	$8.1\cdot10^{-4}$	$1.0\cdot10^{-2}$	$1.0\cdot10^{-2}$	$1.0\cdot10^{-2}$
182	$1.2\cdot10^{-4}$	$1.0\cdot10^{-4}$	$1.1\cdot10^{-4}$	$7.6\cdot10^{-3}$	$6.4\cdot10^{-3}$	$7.0\cdot10^{-3}$
187	$10.2\cdot10^{-5}$	$8.4\cdot10^{-5}$	$9.3\cdot10^{-5}$	$1.1\cdot10^{-2}$	$1.2\cdot10^{-2}$	$1.1\cdot10^{-2}$

We wish to express our thanks to A. P. Vinogradov and Prof. S. A. Borovik for their advice, and in addition we want to thank our coworker M. M. Farafanova who did some of the analysis.

Received July 9, 1954

[1]) Mean relative error = 6.3%. Sensitivity of determination by the method developed for Li = 3.10^{-6}%, for Sr = 1.10^{-5}%.

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DETERMINATION OF POTASSIUM WITH SODIUM TETRAPHENYLBORATE

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Sodium tetraphenylborate $Na[B(C_6H_5)_4]$ gives with potassium ions a white bulky, fine crystalline precipitate of $K[B(C_6H_5)_4]$, which is insoluble even in dilute (0.1 N) mineral acids. Potassium can therefore be determined by means of this reagent in acid media in the presence of a number of other cations and anions such as Li^+, Mg^{2+}, Ca^{3+}, Sr^{2+}, Ba^{2+}, Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-}, ClO_4^-, etc. The conversion factor (0.1091) to potassium from the borate is comparatively low, so that permissible errors are levelled down and even small amounts of potassium can be determined with great accuracy [1,2]. The fact that the reagent is not readily available, however, prevents its more widespread use in practice. Results are given in the present paper of gravimetric and volumetric determinations of potassium with sodium tetraphenylborate which was prepared by a simpler method which makes the reagent much more readily available.

Synthesis of Sodium Tetraphenylborate. To a solution of phenylmagnesium bromide prepared from 9.6 g magnesium and 60 g bromobenzene in 200 ml absolute ether cooled with water, is slowly added with vigorous stirring 8.8 g of the molecular compound of boron trifluoride and ether (b.p. 125-129°), dissolved in 30 ml absolute ether [3]. The reaction is carried out in a half-liter three-necked flask fitted with a reflux condenser, a dropping funnel, and a mechanical stirrer. It is best to use ground glass joints for the flask. An excess of phenylmagnesium bromide as shown by the appropriate color reaction [4] should be present. The reaction mixture is heated for 2 hours on a water bath. The ether is then removed under vacuum and the mixture heated on the water bath to boiling and the temperature maintained for 15-20 minutes at this temperature. The reaction mixture is cooled with water and 400-500 ml water added to it. If the temperature should rise, then the flask should be cooled again. A precipitate of magnesium fluoride separates out and a quantity of oily material comes to the surface. This solidifies when the reaction mixture is poured onto a flat dish. 45 g of sodium carbonate dissolved in a small volume of water cooled to room temperature is added to precipitate the magnesium. In order to facilitate filtration and to decolorize the solution, activated charcoal is added before filtration. The precipitate is difficult to wash so that it is best to strip it off the filter, mix it up with 400 ml of water and filter it again. Both filtrates are combined and saturated with sodium chloride. A white, bulky, precipitate of sodium tetraphenylborate settles out, which is filtered off, washed with saturated sodium chloride and dried in a vacuum desiccator over calcium chloride. The yield is ca. 30 g of raw material. This is extracted for 4-6 hours with absolute ether in a Soxhlet apparatus in order to remove impurities which interfere with potassium determinations. After extraction, ca. 26-28 g of material is obtained containing 45-50% of sodium tetraphenylborate, which corresponds to 55-60% of the theoretical, calculated on the boron trifluoride.

The reagent thus prepared is not completely pure and in addition to a

residue which is insoluble in water also contains water-soluble material. It should be made clear, however, that these materials do not interfere with the use of this reagent for gravimetric and volumetric determination of potassium.

The product is dissolved in water at room temperature. It is assumed that it contains ca. 50% sodium tetraphenylborate. A comparatively large residue thus remains undissolved and in order to coagulate this better, 1-2 ml of 0.1 M $Al(NO_3)_3$ is added, and the residue filtered (it is best to filter on the following day). The concentration of sodium tetraphenylborate in the solution thus obtained is determined by precipitation with excess potassium chloride under the identical conditions subsequently used for potassium precipitation.

A standard solution of chemically pure potassium chloride, the strength of which has been accurately determined, was used for standardizing the sodium tetraphenylborate reagent. In order to avoid errors connected with the use of burets, pipets, etc., 5-10 g of this solution was weighed out. The solution was acidified with acetic acid. The optimum pH of the solution should be 3-6 [1]. Some authors [5] prefer to precipitate in more acid solution, e.g., 0.1 N mineral acid solution. It has been found, however [1], that a decrease in pH leads to high results because of precipitation of decomposition products of the acid itself [$HB(C_6H_5)_4$]. Elevated temperatures lead to the same result. The test solution should therefore not be heated above 40°.

The following procedure can be recommended for the gravimetric determination of potassium.

Analytical Procedure. An aliquot of test sample 2-50 mg is transferred to a 100-150 ml beaker and diluted with an amount of water such that after precipitation from a solution containing 2 mg of potassium the final volume is ca. 10 ml, while for precipitation from a solution containing 50 mg, the volume is 70-100 ml. It is recommended that not more than 50 mg of potassium be used because of the bulkiness of the potassium tetraphenylborate formed. Acetic acid is then added in such an amount that at the end point its concentration in solution is 0.5-1%. The beaker plus test solution are heated on a water bath to 40°, when a 3.4% solution of sodium tetraphenylborate is added dropwise in 1.25-1.5 excess. The precipitate settles out comparatively quickly and after 10 minutes it can be filtered through a No. 4 glass or porcelain filter. The precipitate should not be left for more than 1-1.5 hours since long standing leads to high results, probably as the consequence of decomposition of $H[B(C_6H_5)_4]$. The solution is cooled to room temperature before filtration. The precipitate is transferred to the crucible by washing with small aliquots of liquid containing 1% acetic acid and 4 ml reagent/100 ml. (10-30 ml of the wash solution is required); finally the precipitate is washed three times with small amounts of water, 1-5 ml. The precipitate is dried at 110-120° for 1/2-1 hour and then weighed. The potassium value is obtained by multiplying the weight of precipitate by 0.1091.

The results we obtained for potassium are given in Table 1. In experiments 9, 10, 11, potassium was precipitated in the presence of ten times its amount of Mg, Ca, and Ba. These results can be regarded as completely satisfactory. In each case they are not inferior to those obtained by other workers using recrystallized reagents. This shows that the reagent as we prepared it is good enough for the determination of potassium, and that its recrystallization from methylal and chloroform is unnecessary. Moreover the recrystallized reagent is not completely soluble in water, as is evident from published results [1-5], a fact which we verified in our own case.

Volumetric Determination of Potassium

The volumetric method of determining potassium which we are putting forward is based on the precipitation of potassium by excess of a standard solution of sodium tetraphenylborate as in Rudorf and Zannier's method [6], but excess reagent

TABLE 1

Precipitation of Potassium with Sodium Tetraphenylborate

Expt. No.	KCl solution taken, in g	$K[B(C_6H_5)_4]$ precipitated, in mg	K taken, in mg	K found, in mg	Error, in %	Notes
1	1.9765	65.9	7.16	7.19	+0.41	
2	1.9770	66.2	7.23	7.22	−0.13	
3	4.9614	169.7	18.65	18.61	−0.21	
4	4.9604	169.6	18.65	18.61	−0.21	
5	4.9912	192.7	20.98	21.02	+0.19	
6	4.9754	192.5	20.92	21.00	+0.38	
7	5.0027	192.3	21.03	20.98	−0.28	
8	9.9897	387.9	42.16	42.31	+0.35	
9	4.9859	194.5	21.10	21.22	+0.56	$MgSO_4$ added
10	4.9936	199.9	21.13	21.26	+0.62	$Ca(NO_3)_2$ added
11	4.9686	193.5	21.03	21.11	+0.33	$BaCl_2$ added

in our case is determined by titration with ammonium chloride and not with silver nitrate.

Test solution containing potassium as chloride, sulfate, or nitrate is acidified with 0.05 N HCl in such amount that after addition of the respective amount of ca. 0.05 N $Na[B(C_6H_5)_4]$ for precipitation of potassium, the solution has an acid reaction. Precipitation is carried out at room temperature and after 10 minutes the precipitate of potassium tetraphenylborate is filtered by suction through a filter crucible (sintered glass crucible No. 4). A solution of ammonium chloride is then added to the filtrate and the precipitate of ammonium tetraphenylborate thus formed also filtered off. Excess ammonium chloride is determined in the final filtrate by Krapivina's method [7,8]. Precipitation of excess sodium tetraphenylborate with ammonium chloride without preliminary filtration of the potassium precipitate, i.e., simultaneous filtration of potassium and ammonium tetraphenylborate, cannot be recommended, since when such a combined precipitate is allowed to stand the ammonium ions which are in solution start to replace the potassium ions in the precipitate, so that variable results are obtained when the excess ammonium is determined.

Analytical Procedure

Solutions required and their standardization:

1. 0.05 N HCl.
2. 0.05 N NaOH, free of carbonate.
3. Ca. 0.05 N solution of sodium tetraphenylborate prepared as described above by dissolving ca. 17.4 g $Na[B(C_6H_5)_4]$ in 1 liter of water. Before filtration, 5 ml of 0.1 M $Al(NO_3)_3$ is added to the solution to facilitate coagulation of the insoluble precipitate and increase the storage properties of the solution.
4. Ca. 0.03 N NH_4Cl prepared by dissolving 1.9 g NH_4Cl in 1 liter water. The NH_4Cl content is established by titration with 0.05 N NaOH by Krapivina's method [7,8].

To 20 ml of NH_4Cl solution is added a drop of methyl red and the solution neutralized with 0.05 N NaOH, 5 ml of 40% formaldehyde neutralized beforehand is then added, and the hydrochloric acid thereby liberated titrated with 0.05 N NaOH, using phenolphthalein as indicator. Methyl red does not interfere with this titration since it is decolorized before the phenolphthalein color appears.

The ratio of the concentration of NH_4Cl and $Na[B(C_6H_5)_4]$ must be determined also. To do this 15 ml of 0.05 N $Na[B(C_6H_5)_4]$ is added to 20 ml of 0.03 N NH_4Cl acidified with 2 ml of 0.05 N HCl. The precipitate of $NH_4[B(C_6H_5)_4]$ is filtered off (best by suction under vacuum) and washed 3 times with 5 ml of water. The filtrate is neutralized with 0.05 N NaOH, using methyl red as indicator; 5 ml of a neutral solution of 40% formaldehyde is then added, and the acid liberated titrated with 0.05 N NaOH; the excess NH_4Cl is thereby determined.

Determination of Potassium. To 5-10 ml of test solution containing ca. 20 mg potassium is added 2 ml of 0.05 N HCl and 15 ml of ca. 0.05 N $Na[B(C_6H_5)_4]$. The precipitate formed is filtered by suction after 10 minutes and then washed three times with 5 ml of water. 20 ml of ca. 0.03 N NH_4Cl is added to the filtrate, and the precipitate of $NH_4[B(C_6H_5)_4]$ which separates also filtered off after another 10 minutes and washed three times with 5 ml lots of water.

The filtrate is neutralized to the methyl red end point, 5 ml of formaldehyde solution is added, and the mixture titrated with 0.05 N NaOH to the red color of phenolphthalein. In order to calculate the potassium content it is necessary to know the standard titer of the NH_4Cl, which can be established if we have a knowledge of the potassium content of the test solution.

An Example of the Method of Calculation Employed. 13.6 ml of NaOH was used to titrate 20 ml of NH_4Cl. During titration of excess NH_4Cl on precipitation of 15 ml $Na[B(C_6H_5)_4]$ with 20 ml NH_4Cl, 2.85 ml of NaOH was used. From this it follows that 15 ml $Na[B(C_6H_5)_4]$ is equivalent to 13.6 ml − 2.85 ml = 10.75 ml NaOH or 15.81 ml NH_4Cl.

For titration of excess NH_4Cl in the case: test sample + 15 ml $Na[B(C_6H_5)_4]$ + 20 ml NH_4Cl, 12.7 ml of NaOH was used, which is equivalent to 18.63 ml of NH_4Cl. From this it follows that 20 ml − 18.68 ml = 1.32 ml of NH_4Cl has been used for the precipitation of excess $Na[B(C_6H_5)_4]$. For the precipitation of potassium during the analysis, $Na[B(C_6H_5)_4]$ equivalent to 15.81 − 1.32 ml = 14.49 ml NH_4Cl was used. Knowing that the aliquot of solution in this particular case contains 18.67 mg potassium, we can calculate that 1 ml of ca. 0.03 N solution of NH_4Cl corresponds to 18.67/14.49 mg potassium = 1.289 mg. NH_4Cl is thus standardized against chemically pure KCl. Knowing this titer, we can therefore in any case calculate the amount of potassium in the test sample from the number of ml of NH_4Cl used. The NH_4Cl titer should be checked every 2-3 days.

TABLE 2

Volumetric Determination of Potassium with Sodium Tetraphenylborate

Expt. No.	NH_4Cl, in ml	K found, in mg	K taken, in mg	Error, in mg	Error, in %
1	14.61	20.87	20.97	−0.10	0.48
2	14.67	20.96	20.94	+0.02	0.10
3	14.73	21.05	20.94	+0.11	0.52
4	14.73	21.05	20.94	+0.11	0.52
5	14.61	20.87	20.97	−0.10	0.48
6	14.49	20.77	20.84	−0.07	0.33
7	14.55	20.85	20.91	−0.06	0.29
8	14.67	21.03	21.05	−0.02	0.10
9	14.55	20.85	20.87	−0.02	0.10
10	14.61	20.94	20.94	0	0

Results are given in Table 2 for the titration of two series of solutions of chemically pure potassium chloride. The reagent solutions were prepared

separately for each series. These results show that our proposed volumetric method for determination of potassium gives satisfactory results and is not less accurate than the gravimetric method. Its main advantage as compared with the methods of Rudorf and Zannier is that it does not need silver nitrate.

SUMMARY

1. A simplified synthesis of sodium tetraphenylborate has been worked out.

2. It has been shown that the reagent as prepared by our method is suitable for gravimetric determination of potassium.

3. A new volumetric method of determining potassium is described.

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RAPID METHODS OF MICRO ELEMENTAL ANALYSIS

VIII. SIMULTANEOUS MICRO DETERMINATION OF CARBON, HYDROGEN AND PHOSPHORUS IN ORGANO-PHOSPHORUS COMPOUNDS CONTAINING C, H, O, P AND N

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INTRODUCTION

The chemistry of organo-phosphorus compounds has received even wider development in recent years. In addition to research on natural phosphorus-containing compounds and the necessity of controlling the phosphorus content of commerical samples, many scientific-research laboratories need rapid, reliable, and universally applicable analytical methods for phosphorus which do not require large amounts of test material.

The principles of determining phosphorus in organic compounds have been worked out for as long as 50 years. All the methods which are in use at present for the analysis of organo-phosphorus compounds can be divided into three stages: 1) mineralization, 2) quantitative separation of phosphorus in a particular chemical form, and 3) determination of the amount of this particular compound.

One very characteristic feature of organic phosphorus compounds becomes apparent immediately one tries to mineralize them — this is their stability. These compounds, particularly when C—P bonds are present in the molecule, exhibit a marked resistance to oxidizing agents and to temperature.

The most widely used method of mineralizing these compounds is mineralization with liquid oxidizing agents. The following mixtures are those most commonly used: $H_2SO_4 + K_2Cr_2O_7$; $KMnO_4 + HNO_3$; $H_2SO_4 + HNO_3$; and also K_2SO_4, $K_2S_2O_8$, $CuSO_4$, $Al_2(SO_4)_3$, Se. Although the oxidation conditions are very severe — high temperature, a long heating period (for tens of hours), and numerous repeat oxidations —, nevertheless one still comes across examples of incomplete mineralization [1].

Resort is often made to mineralization by fusion with certain alkaline reagents. These methods, however, quite often do not give quantitative breakdown of the test material [2]; during treatment in unsealed vessels loss of phosphorus is a possibility [3].

When the compound has eventually been successfully mineralized, the purely inorganic part of the analysis has to be carried out, viz., quantitative isolation of the ionic phosphorus (usually as the PO_4^{3-} ion) in a chemical form which is suitable for analytical purposes. Even if the method of determination chosen, e.g., a volumetric or colorimetric one, does not require actual isolation of the compound of interest, the final solution after mineralization contains such a variety of interferring ions in fairly large amounts that it is preferable to isolate the phosphorus-containing ion quantitatively from all the others. Hiterto the most specific precipitant for PO_4^{3-} ions has been ammonium molybdate,

which forms an insoluble complex $(NH_4)_3PO_4 \cdot 12MoO_3$. The latter is attractive to chemists because of its very advantageous conversion factor. The ratio of its molecular weight to the phosphorus it contains is 68:1. In micro-analysis it is possible to weigh a precipitate with such a composition on ordinary analytical balances [4]. The advantage given by the factor is, however, counteracted by the negative qualities of the complex; viz., changes in composition with precipitation conditions, composition of solution, treatment and drying of precipitate [5], the long and meticulous operations required during separation of the precipitate. In order to make the molecule even bigger, its capacity to combine with certain organic bases is also used; e.g., strychnine [6], hydroxyquinoline [7], quinine [8], antipyrine [9]. For rough determinations with accuracies of the order of $\pm 5\%$; centrifuging the precipitate and comparing its volume with that of a precipitate prepared in the same way from solutions containing known concentrations of PO_4^{3-} ions [10] is adequate.

The amount of ammonium phosphomolybdate is often determined gravimetrically, but it can also be titrated directly with alkalies, or excess of the latter may be determined after dissolving the phosphomolybdate precipitate in the alkali [11]. The amount of phosphorus in it can also be indirectly determined from its nitrogen content as determined by the Kjeldahl method [12] or from the amount of molybdenum determined polarographically [13]. When the precipitate is treated with a reducing agent ($SnCl_2$ + HCl, fresh $FeSO_4$, 1-amino-2-naphthol-4-sulfonic acid, hydrazine sulfate, hydroquinone, citric acid) [14], it is brought into solution as a colored complex: molybdenum blue, the amount of which is determined colorimetrically [15]. Methods have been worked out in which, on the one hand the specificity of ammonium molybdate is used, while on the other hand the difficulties connected with the separation of the phosphomolybdate precipitate are avoided. The precipitate is dissolved in ammonia and reprecipitated as $MgNH_4PO_4 \cdot 6H_2O$, which is calcined to magnesium pyrophosphate $Mg_2P_2O_7$ (when precipitation is carried out directly after mineralization, it is very difficult to achieve quantitative precipitation [16]). The colored complexes formed by the PO_4^{3-} ion with salts of vanadium [18] and cobalt [17] have also been used for colorimetric determination of phosphorus. Its concentration can be determined by amperometric determination with trivalent iron [19], and by titration with uranium salts [20] or cerium salts [21].

Physico-chemical methods of analysis usually find limited application because of insufficient accuracy. Most colorimetric methods can only be used for samples with low phosphorus contents or for trace determinations. In none of the methods indicated is the quantitative formation of phosphorus pentoxide in an atmosphere of oxygen used for the direct gravimetric determination of phosphorus in organo-phosphorus compounds. Moreover, no method has been developed for the simultaneous determination of other elements present as well as phosphorus.

Our problem was to develop a method based on new principles which would permit phosphorus to be determined rapidly and accurately, simultaneously with other elements; for this it was necessary to find more suitable conditions for the quantitative breakdown of organo-phosphorus molecules and to isolate phosphorus in a weighable form. This would lead on the one hand to reducing the time of a determination, and open up possibilities of simultaneous determination of other elements.

DEVELOPMENT OF THE METHOD

As a first step we tried to analyze compounds containing C, H, O, P and N. We tried a combustion method worked out in the Micro-Analytical Laboratory of the Institute of Organic Chemistry, Academy of Sciences, USSR [22] for the analysis of the test organo-phosphorus compounds. The test material was pyrolyzed in a small open quartz beaker placed in a quartz tube, the pyrolysis products being burned in a rapid stream of oxygen. Under these conditions the phos-

phorus of organo-phosphorus compounds is converted into phosphorus pentoxide [23]. Experiment showed, however, that it is difficult to determine phosphorus pentoxide as an ash remaining in the beaker, since, on the one hand, phosphorus pentoxide is extremely hygroscopic so that its weight varies, while on the other hand, because of its volatility it penetrates into the water and carbon dioxide absorption tubes, thereby upsetting the balance of all three elements — C, H and P. Apart from this, phosphorus pentoxide forms a thin coating around the carbon residue obtained as a result of pyrolysis, and this film prevents combustion of the carbon. Another undesirable feature of phosphorus pentoxide is its corrosive action on quartz.

In order to prevent volatilization of phosphorus pentoxide from the small quartz beaker and formation of a film around the carbon, we decided to use an internal absorbent; the aliquot of test material in a small beaker was accordingly strewn with a layer of a preparation with special properties. Thus such a preparation should be thermally stable under the combustion conditions employed, should react quantitatively with phosphorus pentoxide to form a stable compound, and at the same time should be indifferent to the other products of pyrolysis and combustion.

We tried out purified fibrous asbestos and granulated magnesium oxide. These materials have already justified their use fairly well for the analysis of such difficult-to-analyze materials as fluoro- and silico-organic compounds [24, 25]. We found, however, that the use of asbestos impregnated with vanadium pentoxide V_2O_5 [26] gave no better results than pure asbestos. Both asbestos and magnesium oxide can be used to determine phosphorus by their increase in weight as a result of phosphorus pentoxide take-up, but the results are not accurate enough. It is difficult to get both these materials to constant weight by calcining, they corrode the quartz tube, and because of their hygroscopicity [27], it is difficult to establish the correction to be applied in blank tests when they are strewn over the test material. When it is taken into account that only 1.0-1.5 mg of phosphorus pentoxide is formed from the normal amount of sample taken for analysis, the corrections to be applied vary from 100-200 μg, which mean a large error in phosphorus determinations. Nevertheless for the analysis of fluoro- and silico-organic compounds, in view of their special properties, more satisfactory absorbents than magnesium oxide and asbestos have not yet been found.

For analysis of organo-phosphorus compounds we tried to find materials which have a zero correction, i.e., materials which are non-hygroscopic. Pumice is a material which, while similar to asbestos in composition, differs from it in its physical structure; pumice has a large surface because of its porous character, but it is non-hygroscopic like fibrous powdered asbestos. When ground it is easy to transfer from one beaker to another; on calcining it rapidly attains a constant weight, and it does not corrode quartz.

Combustion of organo-phosphorus compounds in which pumice was used showed that the phosphorus pentoxide formed quantitatively during combustion is completely retained by the pumice placed in a small beaker; it is also possible to determine carbon and hydrogen simultaneously. We became convinced as the result of our tests that in order to achieve complete combustion of the test compound it is essential to have an excess of oxygen in the tube.

Preparation of Pumice

Pumice lumps are gradually milled down and a fraction with particle size of ca. 1 mm sieved off. The granules are treated with approximately 30% hydrochloric acid for 3-4 hours in round-bottomed flask on a boiling bath. They are then boiled a few times with water until there is no chloride left in the wash water. The air-dried pumice is calcined first in a muffle and then in a quartz tube at 900° in a stream of dry oxygen for ca. 8 hours. The material is kept in a flask fitted with a rubber stopper.

TABLE

Simultaneous Determination of Carbon, Hydrogen and Phosphorus

Expt. No.	Material	Weight taken, in mg	CO_2, in mg	H_2O, in mg	P_2O_5, in mg
1	$(C_6H_5)_3P$	4.815	14.555	2.470	1.280
	C–82.42; H–5.76; P–11.82	4.567	13.780	2.320	1.258
2	$(C_6H_5)_3CPO(OC_4H_9\text{-}i)_2$	3.399	9.193	2.268	0.568
	C–74.29; H–7.62; P–7.09	6.301	17.167	4.157	0.995
3	$(C_6H_5)_3CPO(OCH_3)_2$	5.493	14.366	2.835	1.101
	C–71.57; H–6.01; P–8.79	5.253	13.760	2.970	1.037
4	$C_6H_5NPC_2H_5(OC_2H_5)_2$	6.300	13.721	4.660	1.852
	C–59.73; H–8.36; P–12.84	5.490	11.932	4.130	1.622
5	$(C_6H_5)_3CPO(OC_3H_7\text{-}i)_2$	4.288	11.579	2.650	0.757
	C–73.51; H–7.16; P–7.58	5.702	15.314	3.390	0.991
6	$(CH_3)_2(CH_3CONH)CPO(OC_2H_5)_2$	7.470	12.501	5.687	2.240
	C–45.56; H–8.50; P–13.06	8.109	13.596	6.144	2.386
7	$CH_3COHNCH(C_6H_5)PO(OC_2H_5)_2$	5.112	10.224	3.306	1.263
	C–54.73; H–7.07; P–10.86	9.099	18.300	5.752	2.259
8	$(C_4H_9O)_2POCON(C_2H_5)_2$	3.951	7.749	3.427	0.971
	C–53.22; H–9.63; P–10.56	4.601	8.992	4.043	1.118
9	$(C_6H_5)NHCONHCH(C_6H_5)PO(OC_2H_5)_2$	7.455	16.256	4.239	1.457
	C–59.66; H–6.41; P–8.54	6.140	13.452	3.580	1.219
10	$(C_2H_5)_2NCOPO(C_2H_5)OC_4H_9$	4.947	9.592	4.350	1.389
	C–52.99; H–9.70; P–12.44	3.450	6.698	3.008	1.001

Analytical Procedure

Pumice thus prepared is loaded into the usual small quartz beaker used for combustion until its level after gentle tapping of the sides of the beaker is ca. 10 mm from the top; the beaker is wiped with shammy and passed through the oxidizing flame of a burner before placing it in a combustion tube of the set-up used for micro-determination of C and H; a second beaker is then placed in the combustion tube. The tube is sealed with corks and an electric oven moved on to the beaker + pumice, an absorption train for carbon dioxide, nitrogen oxides (if there is nitrogen in the test material) and water is then connected to the tube. 500 ml of oxygen is passed through the tube. The electric furnace is moved off, the absorption apparatus disconnected, wiped, and then transferred to the balance; the beakers are next removed from the tube, placed on a block and transferred to the balance also. The apparatus is weighed 15 and 20 minutes afterwards, and then connected up again to the combustion apparatus; about 6-8 mg of test material is placed in the empty quartz beaker (or a capillary containing the test material if it is liquid) and strewn with pumice from the other beaker. The total weight of beaker + aliquot of sample + pumice (taking into account the zero point of the balance) is taken at the 25th minute from the moment when the beaker containing the pumice was withdrawn from the combustion tube. Combustion is carried out in an oxygen stream, the throughput of which is 30-35 ml/minute.

When combustion is complete and when no more black zones of carbon are formed on the pumice on bringing the burner flame to the place where the sample

TABLE (continued)

Expt. No.	% C	Δ % C	% H	Δ % H	% P	Δ % P
1	82.49	+0.07	5.76	0	11.62	−0.20
	82.34	−0.08	5.67	−0.08	12.02	+0.20
2	74.33	+0.04	7.47	−0.15	7.29	+0.20
	74.35	+0.06	7.38	−0.24	6.89	−0.20
3	71.37	−0.20	5.76	−0.23	8.77	−0.02
	71.48	−0.09	6.33	+0.32	8.62	−0.17
4	59.43	−0.30	8.28	−0.08	12.83	−0.01
	59.51	+0.22	8.42	+0.06	12.89	−0.05
5	73.70	+0.19	6.92	−0.24	7.71	+0.13
	73.31	−0.20	6.65	−0.51	7.56	−0.02
6	45.67	+0.11	8.52	+0.02	13.09	+0.03
	45.75	+0.19	8.48	−0.02	12.84	−0.22
7	54.58	−0.15	7.24	+0.17	10.78	−0.08
	54.89	+0.16	7.07	0	10.84	−0.02
8	53.52	−0.30	9.71	+0.08	10.73	+0.17
	53.33	−0.11	9.83	+0.20	10.60	+0.04
9	59.51	−0.15	6.36	−0.04	8.53	−0.01
	59.79	+0.13	6.52	+0.11	8.67	+0.13
10	52.91	−0.08	9.84	+0.14	12.26	−0.18
	52.98	−0.01	9.76	+0.06	12.65	+0.21

is located, the end of the beaker is thoroughly heated, the burner is then moved away and the beaker allowed to cool for 5 minutes (with the oxygen still switched on). Next the electric oven is used to heat the tube for another 5 minutes. The operation is repeated. The oven is finally removed and the boat allowed to cool a little. The cork of the combustion tube is removed, and the oxidizing flame of the burner played up and down the length of the tube 2-3 times. The beaker is carefully removed, care being taken to see that no pumice falls out of it. The procedure is then the same as at the beginning of the analysis: the absorption apparatus is weighed at 15 and 20 minutes, and the boat at the 25th minute after removal of the beaker, etc., from the combustion tube. The increase in weight as a result of absorption of phosphorus pentoxide is calculated from the change in zero of the balance during the time of the experiment.

Calculation of Results

Carbon and hydrogen are calculated as usual, while phosphorus is calculated by means of the formula:

$$\% \, P = \frac{a.f}{S} \cdot 100$$

where a is the increase in weight as a result of phosphorus pentoxide absorption; this is taken as the difference between the weight of the boat after combustion and before combustion (after deducting the weight of sample taken); f is the conversion factor = $2P/P_2O_5 = 0.4364$; S = weight of aliquot.

DISCUSSION OF RESULTS

The method proposed represents a great saving of time because two of the steps mentioned in our opening remarks are combined into one, viz., mineralization, which occurs under exceptionally suitable conditions in our method, and the isolation of phosphorus in a particular chemical form; the third stage — determination of this chemical form — reduces to simple weighing of the beaker immediately after combustion. The combustion conditions employed permit carbon and hydrogen to be determined simultaneously with the normal accuracy for this type of analysis.

The efficiency of the pumice granules under the combustion conditions employed is the result of the cracking action of its large porous surface, and its abundance of sharp edges and corners [28, 29]. The phosphorus pentoxide formed reacts chemically with pumice in the immediate neighborhood where decomposition of the sample occurs. It is not a question of mechanical retention of phosphorus pentoxide fumes here, since phosphorus pentoxide can be normally removed by heating to ca. 300-400°. Pumice contains SiO_2, R_2O (alkaline), Al_2O_3 and iron oxides. All these components are capable of giving thermally stable compounds with phosphorus pentoxide, $SiO_2 \cdot P_2O_5$ is one of the characteristic compounds of phosphorus. A modification of this, silicyl metaphosphate (SiO^{2+}), which forms at the temperature which is developed during combustion (ca. 1000°), is extremely stable. The reaction is equimolar, so that calculations can be made on the basis of an increase in weight in the form P_2O_5.

Pyrolysis of the sample should be effected rapidly, as in the rapid combustion method of Korshun and Klimova [22]. When this is done, the carbon which is evolved is distributed over a large surface, i.e., a thin film is formed which can be burnt off rapidly. Accordingly there is no need to fear that the pyrolysis products will burn near the opening of the beaker. As experiment showed, combustion outside the absorptive layer does not lead to low results for phosphorus. Apparently the volatile pyrolysis products do not contain phosphorus; the latter is converted exclusively into phosphorus pentoxide, which reacts immediately with pumice, as can be observed from the change in color of the latter from rose to grey in the closed end of the beaker.

For most of the compounds we analyzed, it was sufficient to carry out two final heatings with the oven. In some cases, however, particularly for thermally stable compounds, such as the derivatives of triphenylmethylphosphinic acid (see Nos. 2, 3 and 5 in the Table), it was necessary to resort to gradual combustion by moving the burner to and fro several times near the sample. By doing this the sphere of reaction becomes rich in oxygen, thereby leading to complete combustion of the carbonized part of the sample.

Certain precautions must be taken during analysis. When sampling, particularly liquids, greases, and easily electrified solids, care must be taken to see that the liquids do not fall on the walls of the beaker used for combustion far from the bottom, otherwise low results may be obtained for phosphorus content. It must also be remembered that light lumps of pumice are easily electrified at low humidities and may therefore fly out of the container when being placed in, or removed from the combustion tube. The oxidizing flame of the burner is therefore used for discharging it as indicated above.

In analysis for phosphorus only, it is sufficient to have one container for oxygen and a purifying train of 2-3 tubes for combustion. In such cases a series of determinations can be carried out.

All weighings were made on a Russian-made balance — the VM-20, issued in 1953. Although this model is officially regarded as a semi-micro balance, micro analysis can be carried out with it when it is properly used.

At the moment we are successfully developing methods for the simultaneous

determination of C, H, P, and S in phosphorus-containing materials,using only one aliquot.

SUMMARY

A new method has been worked out for simultaneous micro determination of C, H, and P in compounds containing C, H, O, P, and N. One determination takes ca. 1.5 hours. Deviation from theory does not exceed 0.3%.

The advantages of this method are. its rapidity, the possibility of analyzing materials which are not decomposed by other methods, determination of carbon and hydrogen as well as phosphorus on one aliquot, and protection of the quartz apparatus from corrosion.

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ENERGY CHARACTERISTICS AND THE ANALYTICAL CLASSIFICATION OF IONS

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The fundamental energy characteristics of ions which determine their behavior in solution are – the electrostatic characteristic (the quotient, square of the radius divided by the ionic radius – z^2/r) and the electrical nature of the ion in aqueous solution (the covalent characteristic [1]). The first of these characteristics, viz. (z^2/r) determines the electrostatic interaction of a given ion with other ions or dipolar molecules, the second (K) is the tendency of an ion to form covalent bonds. Complete information on these characteristics is given in Table 1.

TABLE 1

Energy Characteristics of Cations

Ions	Ionic radius	$\frac{z^2}{r}$	Covalent characteristic in aqueous solution	Ions	Ionic radius	$\frac{z^2}{r}$	Covalent characteristic in aqueous solution
Singly charged cations							
Li^+	0.78	1.28	–1	Cu^{2+}	0.80	5.00	137
Na^+	0.98	1.02	18	Sn^{2+}	1.17	3.42	–
K^+	1.33	0.75	20	Pb^{2+}	1.32	3.03	156
Rb^+	1.49	0.67	23	Cr^{2+}	0.81	4.94	71
Cs^+	1.65	0.61	22	Mn^{2+}	0.91	4.40	85
Fr^+	1.78	0.56	–	Fe^{2+}	0.83	5.82	86
Cu^+	(0.98)	(1.02)	(30)	Ni^{2+}	0.78	5.12	97
Ag^+	1.13	0.88	57	Co^{2+}	0.82	4.88	93
Tl	1.49	0.67	59				
Doubly charged ions				Triply charged ions			
Be^{2+}	0.34	11.74	55	Al^{3+}	0.57	15.8	121
Mg^{2+}	0.78	5.12	57	Sc^{3+}	0.83	10.8	–
Ca^{2+}	1.06	3.78	34	Y^{3+}	1.06	9.43	54
Sr^{2+}	1.27	3.15	43	La^{3+}	1.22	7.37	37
Ba^{2+}	1.43	2.80	35	Ln^{3+}	0.99–1.18	9.1–7.62	39–54
Ra^{2+}	1.52	2.63	–	Ga^{3+}	0.62	14.5	219
Zn^{2+}	0.83	4.82	135	In^{3+}	0.92	9.80	226
Cd^{2+}	1.03	3.88	159	Tl^{3+}	1.05	8.56	290
Hg^{2+}	1.12	3.57	228	Cr^{3+}	0.64	14.06	151
				Fe^{3+}	0.67	13.42	197
				Bi^{3+}	1.17	7.70	290

On the basis of the values of these characteristics, it is possible to segregate the ions into clearly defined analytical groups. On this basis some new groups appear in addition to those known already. The introduction of these

new groups can be based not only on the respective energy relationships but also on the necessity of expanding further the existing classification so as to include all elements, including the rare elements.

The magnitude of the covalent characteristic (K) of ions in aqueous solution determines the behavior of ions to all reagents containing strongly polarized atoms, including some important reagents such as hydrogen sulfide and ammonium sulfide. All cations can be divided into three groups according to the value of (K).

1. Ions with a low (K), which form sulfides soluble in water or completely decomposed by water to give hydroxides.

2. Ions with average values of (K), which form sulfides insoluble in water but soluble in acids.

3. Ions with a high (K), forming sulfides which are insoluble in acids.

Let us consider the characteristics of these three groups in greater detail.

To the first group belong singly, doubly, and triply charged ions with (K) respectively less than 30, 70 and 190 kcal and also ions with four charges with a low (K):

$$Li^+\ Na^+\ K^+\ Rb^+\ Cs^+\ Fr^+$$
$$Be^{2+}\ Mg^{2+}\ Ca^{2+}\ Sr^{2+}\ Ba^{2+}\ Ra^{2+}\ (Eu^{2+})$$
$$Al^{3+}\ Sc^{3+}\ Y^{3+}\ La^{3+}\ Ln^{3+}\ \ Ac^{3+}\ Cr^{3+}\ (V^{3+},\ Ti^{3+})^{1)}$$
$$Ti^{4+}\ Zr^{4+}\ Hf^{4+}\ Ce^{4+}\ Th^{4+}$$

According to general analytical classification these ions belong to the first two analytical groups of cations and to the first subgroup of the third analytical group.

A characteristic of this group of ions is that they have either a complete electronic structure of the inert gas type, or, where there is a high charge, a small number of 3d electrons (not more than 3).

The second group includes ions with two charges and with a (K) between 70 and 130 kcal, and ions with three charges with a (K) between 190 and 230 kcal:

$$Cr^{2+}\ Mn^{2+}\ Fe^{2+}\ Co^{2+}\ Ni^{2+}\ Zn^{2+}$$
$$Fe^{3+}\ Ga^{3+}\ In^{3+}$$

All these ions belong to the second subgroup of the third analytical group. The ions which belong to this group have an incomplete 3d shell, the number of electrons varying from 4 to 8. Doubly and triply charged ions with an 18 electron shell and a fairly high z^2/r (Zn^{2+}, Ga^{3+}, In^{3+}) belong to this group.

Ions with one, two, or three positive charges and a (K) exceeding 30, 130 and 230 kcal, respectively, belong to the third group. In addition to the usual cations of this group, there are also positively polarized atoms of the elements (cationoids), which do not form simple aquo-ions in aqueous solution, but form anions or complex ions. The oxidation state of the cationoids given below is denoted by Roman numerals:

$$Cu^+\ Ag^+\ Au^+\ Tl^+\ (Hg_2^{2+})$$
$$Cu^{2+}\ Cd^{2+}\ Hg^{2+}\ Sn^{2+}\ Pb^{2+}\ Pd^{II}\ Pt^{II}$$

---

1) Ln – the rare earth (lanthanide)

$$Au^{III}\ Tl^{3+}\ As^{III}\ Sb^{III}\ Bi^{3+}\ Ru^{III}\ Rh^{III}\ Ir^{III}$$
$$Ge^{IV}\ Sn^{IV}\ Mo^{IV}\ Re^{IV}\ Pt^{IV}$$
$$V^{V}\ As^{V}\ Sb^{V}$$
$$Mo^{VI}\ W^{VI}$$

Cations and cationoids which belong to this group have 18 or 18 + 2 electronic structures and structures with incomplete 4d and 5d shells. The exception is Cu^{2+}, which has an incomplete 3d group. Cationoids with an inert gas structure and in an oxidation state greater than 5, in the absence of strongly manifested oxidation properties (V^{V}, Mo^{VI}, W^{VI}), also belong to this group. When the oxidation properties are strongly expressed (Mn^{VII}, Cr^{VI}), the elements concerned do not form thio salts.

The ions enumerated above which have a high (K) belong to the fourth and fifth analytical groups according to normal classification.

The group of ions with mean values of (K) does not include many ions and need not be subdivided into smaller groups. The remaining two groups include a large number of ions and must therefore be subdivided. This subdivision can be carried out on the basis of the values of z^2/r for the ions.

The first group of ions can thus be divided into two subgroups:

1. Ions with values of z^2/r less than 6, which form hydroxides soluble in water or in ammoniacal buffers:

$$Li^{+}\ Na^{+}\ K^{+}\ Rb^{+}\ Cs^{+}\ Fr^{+}\ (NH_4^{+})$$
$$Mg^{2+}\ Ca^{2+}\ Sr^{2+}\ Ba^{2+}\ Ra^{2+}\ (Eu^{2+})$$

Ions of the first two analytical groups belong to this subgroup.

2. Ions with values of z^2/r greater than 6 which form hydroxides insoluble in water and in an ammoniacal buffer:

$$Be^{2+}\ Al^{3+}\ Sc^{3+}\ Y^{3+}\ La^{3+}\ Ln^{3+}\ Ac^{3+}\ Cr^{3+}\ (V^{3+},\ Ti^{3+})$$
$$Ti^{4+}\ Zr^{4+}\ Hf^{4+}\ Ce^{4+}\ Th^{4+}$$

These ions belong to the first subgroup of the third analytical group.

The numerous ions of the first subgroup (first and second analytical groups) can be divided into:

a) Doubly charged ions with an ionic radius greater than 1.05 Å.

$$Ca^{2+}\ Sr^{2+}\ Ba^{2+}\ Ra^{2+}\ (Eu^{2+})$$

These ions are precipitated by ammonium carbonate, oxalate, and sulfate in alcoholic solution. By a suitable choice of reagents it is possible to differentiate these ions further. Sulfate in aqueous solution precipitates cations with radii greater than 1.25 Å, chromate in acetate buffers precipitates ions with radii greater than 1.3 Å, etc. The lead ion has a radius of 1.32 Å and is therefore reminiscent of the ions enumerated under certain conditions.

b) Singly charged ions with a radius exceeding 1.3 Å.

$$K^{+}\ NH_4^{+}\ Rb^{+}\ Cs^{+}\ Fr^{+}$$

These ions are precipitated by very large anions [$PtCl_6^{2-}$, $Co(NO_2)_6^{3-}$, $HC_4H_4O_6^{-}$, $Bi(S_2O_3)_3^{3-}$, etc.]. As in the previous instance it is possible to differentiate these ions further. By using the anions: BiI_4^{-}, SbI_4^{-}, MnO_4^{-}, $SnCl_6^{2-}$, and others, it is possible to precipitate ions with radii greater than 1.49 Å (Rb^{+}, Cs^{+}, Fr^{+}).

In this way, on a basis of the study of the energy characteristics of ions,

we have brought out a new analytical group – the potassium group which has group reagents and possesses all the characteristic features of an analytical group. This group contains the same number of elements as the alkaline-earth metals, the cations included in the new group however are far less widely distributed. The Tl^+ ion (r = 1.49 Å) possesses some properties in common with the potassium group.

After separating the potassium group there still remain outside this group the ions of Li^+, Na^+ and Mg^{2+}, which do not have a group reagent. The Mg^{2+} ion has a fairly high $z^2/r = 5.12$, and in certain features approximates to the first subgroup of the third analytical group (low solubility of its hydroxide, slightly soluble phosphate, arsenate, silicate, etc.). In certain respects the Mg^{2+} ion approximates to the ions of the calcium group (low solubility of the carbonate), which is also explicable on the nearness of the z^2/r of Mg^{2+} and Ca^{2+}.

The number of cations and cationoids with a high (K) is also very large and can be divided into subgroups on the basis of the values of z^2/r. The cations and cationoids in this group can be divided into three main subgroups:

1. Ions with low values of z^2/r – less than 3.3 (singly charged and large doubly charged ions): Cu^+, Ag^+, Au^+, Tl^+, Hg_2^{2+}, Pb^{2+}, Pt^{II}.

These cations form slightly soluble chlorides and belong to the hydrochloric acid subgroup. The rather large doubly and triply charged ions Hg^{2+}, Pd^{II}, Bi^{3+}, which form slightly soluble iodides, border on this group.

2. Ions with average values for z^2/r: Cu^{2+}, Cd^{2+}, Hg^{2+}, Sn^{2+}, Pd^{II}, Bi^{3+}, Tl^{3+}.

3. Cationoids with high values of z^2/r and which form thio salts: Au^{III}, As^{III}, Sb^{III}, Ge^{IV}, Sn^{IV}, Pt^{IV}, Ir^{IV}, Re^{IV}, V^V, As^V, Sb^V, Mo^{VI}, W^{VI}.

In order to form stable thio salts, it is essential not only to have high values for z^2/r but high values of (K). For this reason the Hg^{2+} ion which has a very high value of (K) for a doubly charged ion, forms thio salts although it is not characterized by a high z^2/r. The classification is shown schematically in Table 2.

The charge, radius, and (K) of an ion are determined by its position in the Mendeleev periodic system. The distribution of ions in analytical groups is based on differences in their chemical properties, on differences in their energy characteristics, and, consequently in the final count is determined by their position in the periodic system.

A number of Soviet chemists have pointed out the essentially close connection between analytical classification of the ions and the periodic system. This has been developed in detail, particularly in Blok's work [2,3].

Blok showed that there is definitely a close link between the analytical classification of ions and the periodic law, and widely used a concept of the energy characteristics of the ion – "the total moment" (z/r). In our opinion Blok rather overemphasizes the significance of the electrostatic characteristic (z^2/r) of the ions and underestimates the significance of the covalent characteristic (K). (K) is only brought in indirectly when introducing empirical corrections for each series of ions with similar electronic structures. Blok does not take into account the different oxidation states of an element, but arbitrarily chooses only one of the oxidation states for each element. This choice is based on the fact that "ions which are present in aqueous solutions prepared for analysis are chosen" [3].

We cannot agree with such a proposition since if it is accepted that the consideration of groups of ions depends on the method of preparing material for analysis, then we should have to re-examine the question of the relation between the analytical characteristics of the ions and the periodic law in

TABLE 2

Classification of Cations on the Basis of Energy Characteristics

	Low covalent characteristic $K_I < 30$ $K_{II} < 70$ $K_{III} < 190$			
	Low electrostatic characteristic $z^2/r < 6$			High electrostatic characteristic $z^2/r > 6$
	Large singly charged ions $r > 1.3$ Å	Large doubly charged ions $r > 1.05$ Å	Stable ions	
Group reagents	Na_2PtCl_6 $Na_3[Co(NO_2)_6]$ $NaHC_4H_4O_6$	$(NH_4)_2CO_3$ $(NH_4)_2C_3O_4$ H_2SO_4 (alc.)	None	$(NH_4)_2S$ or NH_4OH
Ions	K^+ NH_4^+ Rb^+ Cs^+ Fr^+	Ca^{2+} Sr^{2+} Ba^{2+} Ra^{2+} (Eu^{2+})	Li^+ Na^+ Mg^{2+}	Be^{2+} Sc^{3+} Y^{3+} La^{3+} Ln^{3+} Ac^{3+} Cr^{3+} (Ti^{3+}, V^{3+}) Ti^{4+} Zr^{4+} Hf^{4+} Ce^{4+} Th^{4+}

	Mean covalent characteristic $70 < K_{II} < 130$ $190 < K_{III} < 230$	High covalent characteristic 30 135 230		
		Low values of $z^2/r < 3.3$	Mean values of $z^2/r > 3.3$	High values of z^2/r
Group reagents	$(NH_4)_2S$	H_2S in acid solution		
		HCl	–	$(NH_4)_2S$
Ions	Cr^{2+} Mn^{2+} Fe^{2+} Co^{2+} Ni^{2+} Zn^{2+} Fe^{3+} Ga^{3+} In^{3+}	Cu^+ Ag^+ Au^+ Tl^+ Pt^{II} Pb^{2+} Hg_2^{2+}	Cu^{2+} Cd^{2+} Hg^{2+} Sn^{2+} Pd^{II} Bi^{3+} Tl^{3+}	Au^{III} As^{III} Sb^{III} Ge^{IV} Sn^{IV} Pt^{IV} Ir^{IV} Re^{IV} V^V As^V Sb^V Mo^{VI} W^{VI}

accordance with changes in the method of preparation for analysis.

Klyachko and Shapiro [4] have pointed out the necessity of using such important characteristics of the element as the ionization potential and electrical nature and indicated in a general way methods of using these characteristics for establishing relations between an analytical classification of the elements and their position in the periodic system. Recently Klyachko proposed, also in a very general way, to use electronegativity as a single chemical energy characteristic. Such an approach has certain of the drawbacks considered already, as well as some definite advantages.

We have tried to indicate all the numerous states of oxidation. With this in view, when several different oxidation states, in the analytical sense, are present, the square enclosing the given element is divided into several parts; in the right hand side the properties of the highest oxidation states are indicated, while on the left hand side the properties of the lowest oxidation states are indicated. We have pointed out that ions formed by one and the same element in various oxidation states sometimes differ from each other more than

ions of two similar elements in the same oxidation state.

Typical elements which form anions distinguished by low values of the ionized atoms and highest oxidation states are concentrated at the top and right of Table 3. Elements of Groups V, VI, and VII in the highest oxidation states form typical anions (the vanadium, chromium, and manganese sub-groups) and also the analogs of iron in the eighth group.

There is a fairly clear division between elements with a low value of (K) which do not form practically insoluble sulfides, and elements with average and high values of (K). These are elements of Groups I, II, III, IV, and V which form inert gas structures or ones with a small number of 3d electrons. Only Cr^{3+} from Group VI belongs to this class. The value of (K) in sub-groups, as a rule, decreases from top to bottom; consequently neither molybdenum nor tungsten form ions precipitated by ammonium sulfide as hydroxides.

The division between the potassium and alkaline-earth groups is very clearly marked. Li^{+}, Na^{+} and Mg^{2+} remain outside the group, but it is possible to make quite a number of conclusions re their analytical properties from their position in the periodic system.

Mg^{2+} lies between Be^{2+} and Ca^{2+} but actually occupies an intermediate position between ions of the second and third analytical groups with respect to some properties (formation of practically insoluble hydroxides, basic carbonates, practically insoluble phosphates and other compounds). In the horizontal series magnesium is alongside sodium, and thanks to this fact has a number of reactions which justifies the allocation of this ion to the first analytical group.

Elements in the middle of the fourth period form ions characterized by mean values of (K). The exception is Cu^{2+}, which is distinguished by a very high (K). Here we have a manifestation of the tendency of (K) to increase with increasing number of d electrons, and for a sharp fall in (K) in an ion with an 18 electron shell.

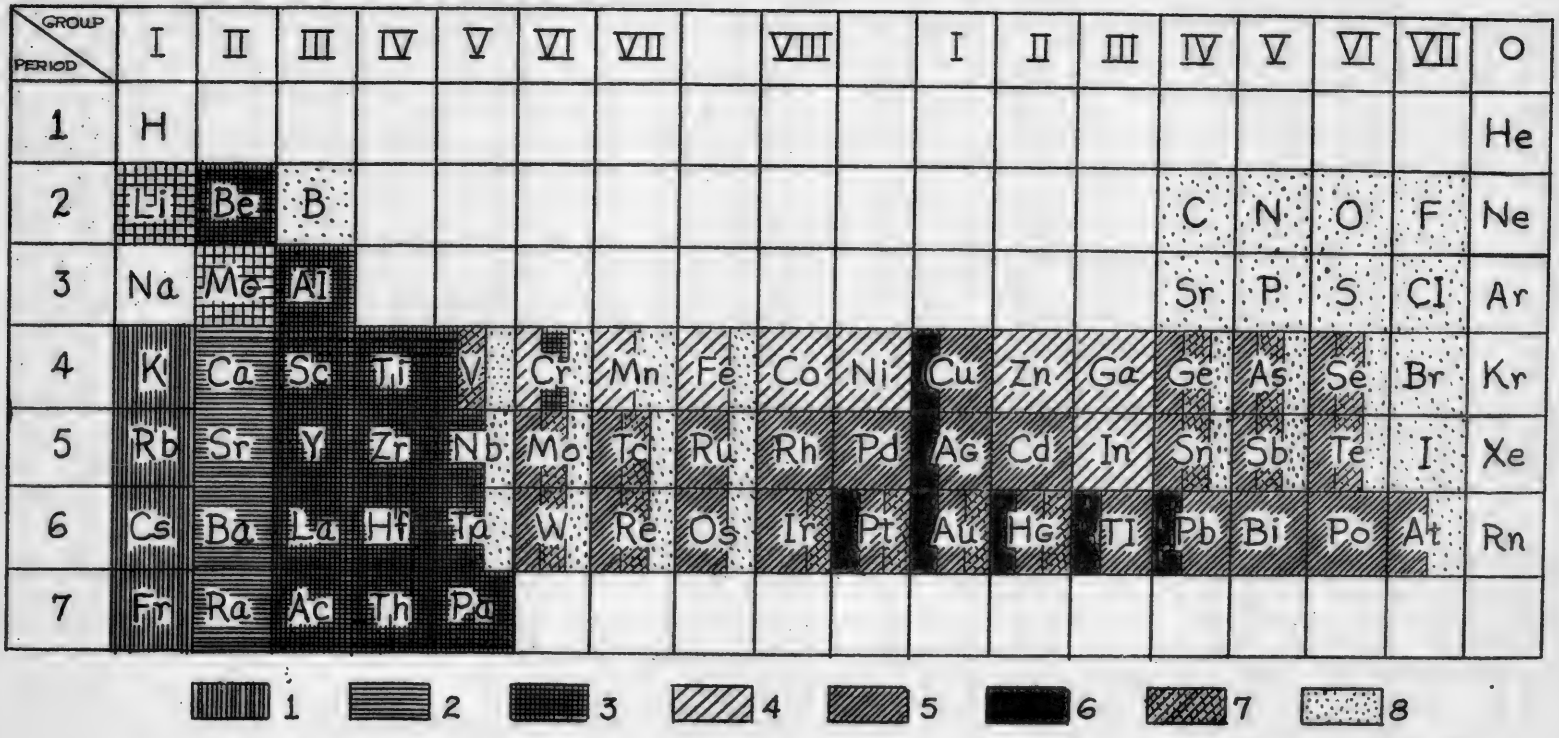
Ions with high (K) which form sulfides insoluble in acids are found mainly in the fifth and sixth periods. In this case we have a tendency for (K) to increase and the covalent character of the bond to strengthen in sub-groups of the Mendeleev system with increasing atomic number.

The formation of practically insoluble chlorides (and also of bromides and iodides) is characteristic of ions with a low charge, fairly large size, and high (K). As a result, ions of elements in the copper sub-group which are in a low state of oxidation, and ions in a low oxidation state but belonging to elements of the sixth period adjacent to the copper group, form insoluble chlorides. In all sub-groups, the sizes of the ions and their (K) increase with increasing atomic number; as a result the solubility of the halides in sub-groups decreases on moving from top to bottom.

Cations and cationoids with high (K) and Z^2/r respectively form thio-salts. The elements which form thio-salts are arranged in the form of three "islands." Certain elements of the sub-group of the V, VI and VII groups [V, Mo, W(Tl), Re] form one "island" — niobium and tantalum do not form thio-salts, apparently because their z_2/r is not high enough; chromium and manganese in the higher oxidation states are characterized by an exceptionally strong oxidizing action. The second "island" is formed by elements in the middle of the sixth period (Ir, Pt, Au, Hg), which are characterized by high (K). Elements mainly of the IV, V and VI groups (Ge, Sn, As, Sb, Se, Te) form the third "island". For the elements of these groups which belong to the sixth period, thio-salt formation is not characteristic, since in this case the higher oxidation states are extremely unstable (clearly expressed oxidizing properties), while ions of the elements in low oxidation states have a low z^2/r.

TABLE 3

Analytical Classification of Ions in D. I. Mendeleev's Periodic System


GROUP
PERIOD
I II III IV V VI VII VIII I II III IV V VI VII O
1 H He
2 Li Be B C N O F Ne
3 Na Mg Al Si P S Cl Ar
4 K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
5 Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
6 Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
7 Fr Ra Ac Th Pa
1 2 3 4 5 6 7 8

1) Singly charged cations precipitated by large anions; 2) doubly charged cation precipitated by sulfate; 3) elements which form practically insoluble hydroxides; 4) elements, which form sulfides insoluble in water, but soluble in acids; 4) elements which form sulfides insoluble in acids; 6) elements, which form practically insoluble chlorides; 7) elements which form thiosalts; 8) elements which form anions.

The behavior of anions in aqueous solution can be interpreted on the basis of the use of their z^2/r and (K) values in just the same way as the behavior of cations in aqueous solutions can be explained on the basis of the use of their energy characteristics.

The basic characteristic which determines the primary division of anions into groups is the magnitude characterizing the tendency of anions to form covalent bonds. Such a quantity is the ionization potential of the anion in aqueous solution — a quantity which is analogous to (K) for a cation and is determined by the energy change during the process:

$$X^-_{(aqueous)} = X^-_{(gaseous)} + e.$$

Unfortunately, the value of the ionization potential in aqueous solution can only be calculted for a limited number of anions [5]. It can be assumed, however, that the tendency to form covalent bonds is determined by the nature of the atom located in the outer sphere and consequently in contact in the crystal lattice with the cations. The ones with the least tendency to have their electrons distorted are hydrogen and fluorine anions. Other atoms are more strongly deformed (nitrogen, sulfur, chlorine, bromine, iodine, etc.). All anions can therefore be divided into two major groups according to this easily established characteristic.

1. Anions which contain oxygen or fluorine atoms in their outer sphere: F^- HCO_2^-, $CH_3CO_2^-$, BO_2^-, NO_2^-, NO_3^-, BrO_3^-, ClO_3^-, IO_3^-, VO_3^-, ClO_4^-, MnO_4^-, ReO_4^-, BF_4^-, CO_3^{2-}, SiO_3^{2-}, HPO_3^{2-}, SO_3^{2-}, SeO_3^{2-}, TeO_3^{2-}, $C_2O_4^{2-}$, SO_4^{2-}, CrO_4^{2-}, SeO_4^{2-}, TeO_4^{2-}, MoO_4^{2-}, WO_4^{2-}, MnO_4^{2-}, FeO_4^{2-}, RuO_4^{2-}, OsO_4^{2-}, SiF_6^{2-}, $S_2O_6^{2-}$, $S_4O_6^{2-}$, $S_2O_8^{2-}$, PO_4^{3-}, AsO_4^{3-}.

Anions of this group are not precipitated by silver ions in acid media.

2. Anions, which contain easily polarized atoms in the outer sphere (nitrogen, sulfur, chlorine, bromine, iodine, etc.) and which form precipitates in acid solution with silver ions: Cl^-, Br^-, I^-, CN^-, CNS^-, $[Cr(NH_3)_2(CNS)_4]^-$, S^{2-}, Se^{2-}, $S_2O_3^{2-}$, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$.

A further subdivision of these anions into groups is possible on the basis of differences in their z^2/r (differences in ionic charges and radii). There is a definite relation between the characteristics of cations and anions during formation of practically insoluble salts [7]: anions with large z^2/r are precipitated by cations with high z^2/r, large anions are precipitated by large cations, etc.

Anions of the first major group noted above can be subdivided into three minor groups:

1. Anions which are precipitated by Mg^{2+} and are characterized by large values of z^2/r. All triply-charged anions and doubly-charged ions with thermochemical radii less than 2 Å belong to this sub-group as well as singly-charged ions with radii less than 1.4 Å: PO_4^{3-}, AsO_4^{3-}, CO_3^{2-}, SiO_3^{2-}, HPO_3^{2-}, F^-.

2. Doubly-charged anions precipitated by Ba^{2+} and characterized by average values of z^2/r. The radii of these anions lie within the limits of 2-3 Å: SO_3^{2-}, SeO_3^{2-}, TeO_3^{2-}, $C_2O_4^{2-}$, SO_4^{2-}, CrO_4^{2-}, SeO_4^{2-}, TeO_4^{2-}, MoO_4^{2-}, WO_4^{2-}, MnO_4^{2-}, FeO_4^{2-}, RuO_4^{2-}, OsO_4^{2-}, SiF_6^{2-}.

3. Anions with low values of z^2/r which are not precipitated by Ba^{2+} and Mg^{2+} ions. Singly-charged ions with radii greater than 1.4 Å, and doubly-charged anions with radii greater than 3 Å: HCO_2^-, $CH_3CO_2^-$, NO_2^-, NO_3^-, BrO_3^-, ClO_3^-, ClO_4^-, MnO_4^-, ReO_4^-, BF_4^-, $S_2O_6^{2-}$, $S_4O_6^{2-}$, $S_2O_8^{2-}$.

BO_2^- and VO_3^- anions should, with respect to their energy characteristics also belong to this group, but it is known that their respective barium salts are only soluble with difficulty. This is explained by the fact that polymerized forms are present in aqueous solution as well as the single ions BO_2^- and VO_3^-.

TABLE 4

Classification of Anions on the Basis of Energy Characteristics

	Anions with fluorine or oxygen atoms in the outer sphere			
	High z^2/r (triply-charged anions, doubly-charged anions with $r < 2$ Å, and singly-charged anions with $r < 1.4$ Å)	Doubly-charged ions with 3 Å $> r >$ 2 Å	Low z^2/r (doubly-charged ions with $r > 3$ Å, singly-charged ions with $r > 1.4$ Å)	
			Large singly-charged ions with $r > 2.2$ Å	Stable ions
Cations of precipitant	Mg^{2+} Ba^{2+}	Ba^{2+}	Rb^+ Cs^+	None
Anions	PO_3^{4-} AsO_4^{3-} CO_3^{2-} SiO_3^{2-} HPO_3^{2-} F^-	SO_3^{2-} SeO_3^{2-} TeO_3^{2-} $C_3O_4^{2-}$ SO_4^{2-} CrO_4^{2-} SeO_4^{2-} TeO_4^{2-} MoO_4^{2-} WO_4^{2-} MnO_4^{2-} FeO_4^{2-} RuO_4^{2-} OsO_4^{2-} SiF_6^{2-}	ClO_4^- MnO_4^- ReO_4^- BF_4^-	HCO_2^- $CH_3CO_2^-$ NO_2^- NO_3^- BrO_3^- ClO_3^-

	Anions with easily polarized atoms in the outer sphere	
	High z^2/r (quadruply-charged ions, triply-charged ions, and doubly-charged ions with $r < 2.3$ Å)	Low z^2/r (singly-charged anions and doubly-charged anions with $r > 2.3$ Å)
Cations of precipitant	Ag^+ in acid solution	
	Zn^{2+}	–
Anions	S^{2-} Se^{2-} $Fe(CN)_6^{3-}$ $Fe(CN)_6^{4-}$	Cl^- Br^- I^- CN^- CNS^- $[Cr(NH_3)_2(CNS)_4]^-$ $S_2O_3^{2-}$

Very large singly-charged anions which form precipitates with large singly-charged cations (Rb^+, Cs^+): ClO_4^-, MnO_4^-, ReO_4^-, BF_4^-, can be distinguished in this sub-group.

The anions of the second major group given above can also be divided into two sub-groups on the basis of the z^2/r values:

1. Anions with high values of z^2/r which are precipitated by zinc ions. Anions with three or four charges as well as anions with two charges and radii less than 2.3 Å belong to this group: S^{2-}, Se^{2-}, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$.

2. Anions with low values of z^2/r which are not precipitated by zinc ions (singly-charged and large doubly-charged anions): Cl^-, Br^-, I^-, CN^-, CNS^-, $[Cr(NH_3)_2(CNS)_4]^-$, $S_2O_3^{2-}$.

This classification is schematically shown in Table 4.

SUMMARY

1. An analytical classification of cations and cationoids on the basis of their energy characteristics is proposed. This classification corresponds to Menshutkin's classification in its most essential features.

2. The relation between the analytical classification proposed and Mendeleev's periodic system is demonstrated.

3. An analytical classification of anions on the basis of their energy characteristics is also proposed.

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A STUDY OF THE POSSIBILITY OF PREVENTING COPRECIPITATION OF COPPER WITH FERRIC HYDROXIDE

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Comparatively little study has been made of chemical methods of preventing coprecipitation in quantitative analysis. The interfering action of certain ions has been used in some cases. Thus, prevention of cation coprecipitation is achieved mainly by the use of ammonium salts and ammonium hydroxide, and also of acids [1]. Organic dyes which are good anion adsorbents may be used for counteracting anion coprecipitation. The issue is, however, not clear cut in all cases [2,3]. In some papers prevention of coprecipitation of contaminants is only touched upon indirectly [4]. In Ostroumov's papers [5], the use of chemical additives leads to a decrease in precipitate surface (formation of crystalline instead of amorphous precipitates), which results in practically complete prevention of adsorption of contaminants. It is possible that one of the reasons for this decrease in coprecipitation of strontium during precipitation of barium chromate in the presence of gelatin may also be a relative shrinking of precipitate surface [6]. Chepelevetsky [7] notes that in the case of coagulation of contaminants during (or after) crystallization, it is expedient to add protective colloids, which prevent contaminants from falling into the precipitate; in cases of adsorption and isomorphism it is possible to apply "masking," in particular, changing the interfering ion into an ion of different valency (e.g., reduction of Fe^{3+} to Fe^{2+}) or into complex ions, which are only sorbed to a very small extent by the precipitate (e.g., conversion of Fe^{3+} into a complex anion).

Our aim was to explain the effect of certain chemical additives on the amount of copper coprecipitated with hydrated ferric hydroxide when ammonium hydroxide is used for precipitating iron (III) from a solution containing iron (III) and copper (II). The work was done under unfavorable conditions, viz., a comparatively high concentration of iron and precipitation in the cold.

EXPERIMENTAL

Known volumes of solutions of $FeNH_4(SO_4)_2$ and $CuSO_4$ were introduced into centrifuge tubes, and certain additives introduced (except in blank tests) and, as a rule, the volume made up with water to approximately 33.5 ml. Iron was then precipitated with ammonium hydroxide in the cold. The precipitate was centrifuged and washed three times with hot NH_4Cl solution and, if necessary, a few more times with hot water. The washed precipitate of hydrated ferric hydroxide was then dissolved in 4 ml of ca. 2 N HNO_3, the iron was again precipitated with NH_4OH (1:1) and centrifuged. The volume of the centrifugate and the wash liquor obtained (the precipitate was washed three times with 5 ml of 2% NH_4NO_3) was made up to 25 ml in a standard flask. 10 ml of this solution was taken and after evaporation until no odor of ammonia was apparent, the copper was titrated amperometrically using the ferrocyanide method [8]. Since the amount of ammonium salts in the titrated solution varied (this was reflected to some extent in the titer of potassium ferrocyanide with copper), we titrated

the copper in the presence of a fairly large amount of ammonium nitrate. This ensured stable conditions and reproducible results. A needle galvanometer (1° = 10^{-6} A) was used for current measurement. The applied potential was 0.5 V. A saturated calomel half element with a large mercury surface was used as reference electrode. The anode was a polarized platinum micro electrode (d ≈ 1 mm, $\frac{1}{d}$ ≈ 3 mm) rotating at 900 rpm. In addition to the test solution, the beaker used for holding the titrating solution also contained 20 ml of 1.5 M CH_3COONa, 0.5 g NH_4NO_3, and water to make up the volume to 40 ml. The whole was titrated against 0.025 M $K_4Fe(CN)_6$ (prepared daily); the latter was standardized against $Cu(NO_3)_2$ and was found to be equivalent to 1.899 mg Cu/ml.

We assumed that all the copper coprecipitated with the ferric hydroxide would appear in solution practically completely during the second precipitation. We also reckoned that the ferric alum in solution would affect the results of all experiments to an equal extent.

TABLE 1

Effect of Certain Additives on Coprecipitation of Copper

Expt. No.	Amount taken in mg		5 ml of saturated alcoholic soln. added	Total volume before pptn in ml	Volume 0.0250 M $K_4Fe(CN)_6$ used in ml	Cu found in ppt. in mg	Copptd. Cu/Cu in %	Copptd. Cu/Fe in %
	Fe	Cu						
1	48.68	18.04	—	26	0.360	1.71	9.5	3.5
2	48.68	18.04	—	26	0.332	1.58	8.7	3.3
3	49.63	18.04	Safranine	31	0.320	1.52	8.4	3.1
4	48.68	18.04	Methyl blue	31	0.313	1.45	8.1	3.0
5	49.63	18.04	" "	31	0.284	1.34	7.5	2.7
6	49.63	18.04	Methyl violet	31	0.340	1.61	8.9	3.2
7	49.63	18.04	" "	10	0.203	0.96	5.3	1.9
8	49.63	18.04	Bismarck brown	31	0.277	1.32	7.3	2.7
9	49.63	18.04	" "	10	0.185	0.88	4.9	1.8
10	48.68	18.04	5% soln. of sodium salt of eosin	31	0.298	1.42	7.8	2.9
11	48.68	18.04	5% gelatin, 2 ml	31.5	0.248	1.18	6.5	2.4
12	48.68	18.04	1% agar-agar	31	0.320	1.52	8.4	3.1
			7.5 ml 4 N soln. added					
13	49.63	18.04	NH_4Cl	—	0.142	0.67	3.7	1.4
14	48.68	18.04	$N(CH_3)_3HCl$	—	0.208	0.99	5.5	2.0
15	49.63	18.04	Pyridine	—	0.259	1.23	6.8	2.5
16	49.63	18.04	Urea	—	0.381	1.81	10.0	3.6
17	49.63	18.04	Urotropine	—	0.353	1.68	9.3	3.4
18	49.63	18.04	"	—	0.150	2.80	15.8	5.7
19	49.63	18.04	NaCl	—	0.254	1.21	6.7	2.4
20	49.63	18.04	KCl	—	0.253	1.20	6.6	2.4

Note 1. In all the experiments the volume before precipitation was ca. 33.5 ml; the NH_4OH (1:1) was not added in excess (6 ml).

2. In experiments 3, 5, 7, 15, 16, 18, the solutions of additives were neutralized with HCl during preparation.

3. In experiment 18, 2.5 ml of the 25 ml was used for titration of the copper.

4. In the results given in this table and in all the remaining experiments, the copper coprecipitated, expressed as a percentage of the total amount of copper taken, is denoted as "Copptd. Cu/Cu in %", while when expressed as a percentage of the iron taken, it is denoted by "Copptd. Cu/Fe in %".

5. In experiments 7 and 9 the dye is destroyed by evaporation with H_2O_2 before titration of the copper.

6. In experiment 10 it is the cation Na^+ which has a retarding effect on the coprecipitation of copper, and not the eosin anion.

7. In experiments 10, 11, and 12, the additives are in aqueous solution, while in the last two, gelatin and agar-agar were added to try and cut down the surface of the $Fe(OH)_3$.

The results in Table 1 show that Bismarck brown was fairly successful in preventing coprecipitation of copper.

The use of dyes in analysis is, however, complicated by their limited solubility.

In practice the most satisfactory results are obtained by combining the action of ammonium salts with NH_4OH.

Table 2 contains results of experiments in which these were used. In particular we could not confirm the correctness of Stromberg, Dityatkovsky and Milovanova's assertions [9] that on precipitation of iron as hydroxide in the presence of Cu^{2+} ions (for definite ratios of these components) in solution with concentrations of NH_4Cl from 0.7-1 N, and of NH_4OH from 2.5-3 N, there is practically no copper adsorption (Table 2, experiment 9). Results are also given in this table of experiments carried out under the conditions recommended by N. A. Tananaev [10] (precipitation in concentrated solution), except that after precipitation it was cold water, and not hot water as the author suggested, that was used. A consideration of the results given in Table 2 shows that an

TABLE 2

Effect of NH_4Cl and NH_4OH on Coprecipitation of Copper

Expt. No.	Amount taken, in mg		Amount of 4 N NH_4Cl added, in ml	Volume of soln before pptn., in ml	NH_4OH added, in ml	Volume 0.0250 M $K_4Fe(CN)_6$ used, in ml	Cu found in ppt., in mg	Copptd. Cu/Cu, in %	Copptd. Cu/Fe, in %
	Fe	Cu							
1	49.63	18.04	7.5	33.5	6 (1:1)	0.137	0.65	3.6	1.3
2	49.63	18.04	7.5	33.5	12 (1:1)	0.070	0.33	1.8	0.7
3	49.63	18.04	7.5	33.5	9 Conc.	0.056	0.27	1.5	0.5
4	49.63	18.04	7.5	33.5	18 "	0.026	0.12	0.7	0.3
5	49.63	18.04	7.5	33.5	20 "	0.045	0.21	1.2	0.4
6	49.63	18.04	7.5	12.55	20 "	0.034	0.16	0.9	0.3
7	49.63	18.04	0.00	4.55	20 "	0.037	0.18	1.0	0.4
8	49.63	18.04	7.5	12.60	20 "	0.033	0.16	0.9	0.3
9	49.63	9.02	7.5	33.5	18 (1:1)	0.035	0.17	1.9	0.3
10	49.63	9.02	0.00	33.5	18 (1:1)	0.076	0.36	4.0	0.7

increased concentration of NH_4OH in solution has a particularly favorable effect in decreasing the amount of Cu^{2+} adsorbed. In this connection it can be postulated that it is the complex-forming capacity of the latter which is chiefly responsible for the prevention of Cu^{2+} ion adsorption, and not the adsorption of ammonium ions and even of NH_4OH molecules (especially if we take into account Chepelevetsky's propositions [7]).

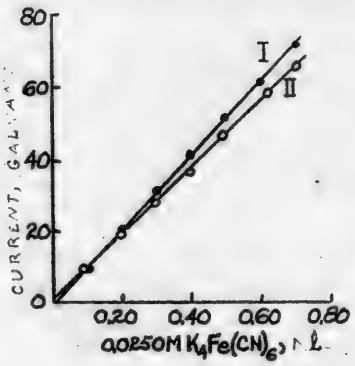
The use of glycine and ethylenediamine, which give even more stable complexes with copper than ammonia, gave good results (see Tables 3, 4 and dia-

gram). In the following series: ammonium hydroxide – glycine – ethylenediamine, the capacity to prevent copper coprecipitation increases with increasing stability of the respective copper complex; this is illustrated by a comparison of the instability constants of the latter [11]:

$$\frac{[Cu^{2+}]\cdot[NH_3]^4}{[Cu(NH_3)_4^{2+}]} = 2.1\cdot10^{-13}$$

$$\frac{[Cu^{2+}]\cdot[NH_2CH_2COO^-]^2}{[Cu(NH_2CH_2COO)_2]} = 5.3\cdot10^{-16}$$

$$\frac{[Cu^{2+}]\cdot[NH_2CH_2CH_2NH_2]^2}{[Cu(NH_2CH_2CH_2NH_2)_2^{2+}]} = 2.5\cdot10^{-20}$$



Titration curves for copper in 10 ml of the second centrifugate after precipitation of iron in the presence of: I – 0.5 g glycine; II – 100 mg ethylenediamine.

It should be noted that if the concentration of complexing agent used is too high, then iron also will form a complex which is not destroyed by ammonium hydroxide (e.g., for a concentration of 0.9 g glycine in 33.5 ml solution). Under the conditions given in Table 3, complex formation with iron is not observed, as proved by qualitative tests on the centrifugate obtained after precipitating 48.63 mg iron in the presence of 18.04 mg coppper in a volume of 33.5 ml. This test was carried out by evaporating small amounts of centrifugate with aqua-regia to destroy the glycine. No Fe^{3+} could be detected in the centrifugate thus treated.

It is also of interest to note that on adding glycine after precipitation of $Fe(OH)_3$ in the presence of Cu^{2+}, only small amounts of Cu^{2+} could be detected in the ferric hydroxide precipitate (Table 3, experiment 8). This confirms the adsorption character of coprecipitation of copper on ferric hydroxide and gives a picture of the mechanism of complex formation. Further work may lead to even better complexing agents.

These experiments showed that complex copper ions are adsorbed to a lesser extent than simple copper ions (or more accurately, aquo complexes). The explanation of this fact is to be sought in the fact that the radii of the first copper ions are bigger (the charge density is smaller) than the latter. It should also be remembered that the formation of inner complex compounds of copper decreases the charge on the complex to an even greater extent. In addition, the aquo complexes throw off the water "coat" comparatively easily, so that the copper ions are enabled to approach nearer to the adsorbing surfaces.

Karaoglanov [12] showed that on precipitation of H_2SO_4 with solutions of $Ba(NO_3)_2$, $BaCl_2$ and BaI_2, coprecipitation of barium decreased from nitrate to iodide. This can also be explained by complex formation, the tendency to which increases from $NO_3^- - Cl^- - I^-$ from left to right. (Coprecipitation is decreased even more if BaI is added in the presence of NH_4I.) Our observation is confirmed by other similar examples adduced by Karaoglanov. It is also confirmed by other results ([1], p. 355).

TABLE 3

Effect of Glycine on Coprecipitation of Copper

Expt. No.	Amount taken, in mg		Glycine added in g	Amount of NH_4OH added in ml	Amount of 0.0250 M $K_4Fe(CN)_6$ used in ml	Cu found in ppt. in mg	Copptd. Cu/Cu in %	Copptd. Cu/Fe in %
	Fe	Cu						
1	49.63	18.04	0.3	6 (1:1)	0.065	0.31	1.7	0.6
2	49.63	18.04	0.4	6 (1:1)	0.033	0.16	0.9	0.3
3	49.63	18.04	0.5	6 (1:1)	0.010	0.05	0.3	0.1
4	49.63	18.04	0.5	6 (1:1)	0.000	0.00	0.0	0.0
5	49.63	18.04	0.5	6 (1:1)	0.011	0.05	0.3	0.1
6	49.63	22.55	0.5	6 (1:1)	0.029	0.14	0.6	0.3
7	49.63	27.06	0.5	6 (1:1)	0.039	0.19	0.7	0.4
8	49.63	18.04	0.4	6 (1:1)	0.015	0.07	0.4	0.1
9	49.63	18.04	0.4	9 Conc.	0.000	0.00	0.0	0.0
10	24.81	27.06	0.4	9 "	0.000	0.00	0.0	0.0

Note 1. In all cases the volume of solution before precipitation was ca. 33 ml. 2. In experiments 8, 9, 10, 1.6 g of NH_4Cl was added. 3. In experiment 8, glycine was added after precipitation of the iron.

TABLE 4

Effect of Ethylenediamine on Coprecipitation of Copper

Expt. No.	Amount taken, in mg		Ethylene-diamine added in mg	Amount of 0.0250 M $K_4Fe(CN)_6$ used, in ml	Cu found in ppt. in mg	Copptd. Cu/Cu in %	Copptd. Cu/Fe in %
	Fe	Cu					
1	49.63	18.04	50	0.008	0.04	0.2	0.1
2	49.63	18.04	50	0.013	0.06	0.3	0.1
3	49.63	18.04	100	0.000	0.00	0.0	0.0
4	49.63	18.04	100	0.000	0.00	0.0	0.0
5	49.63	18.04	100	0.000	0.00	0.0	0.0
6	49.63	18.04	100	0.000	0.00	0.0	0.0
7	49.63	22.55	100	0.000	0.00	0.0	0.0
8	49.63	27.06	150	0.000	0.00	0.0	0.0

Note. In all cases the volume of solution before precipitation was ca. 33.5 ml; NH_4OH (1:1) was not added in excess (6 ml).

The use of complexing agents during the precipitation of $Fe(OH)_3$ in the presence of copper does away with the necessity of a secondary precipitation, simplifies experimental technique, and opens up new possibilities in cases where excess NH_4OH cannot be used (e.g., during the precipitation of Al^{3+}).

In principle it follows that for any coprecipitating ion, it is possible to look for a specific complexing agent which does not act on the precipitated ion, while the interfering cations can be bound up into complex cations also, i.e., conversion of the first into complex anions is not compulsory [7].

Addition of the respective complexing agents, therefore, can be used as a general method for preventing adsorption, although there are grounds for thinking that these can also be useful in preventing such a form of coprecipitation as isomorphism [7].

SUMMARY

1. A study has been made of the effect of certain materials on the amount of copper coprecipitated during precipitation of hydrated ferric hydroxide with ammonium hydroxide from solutions containing Fe^{3+} and Cu^{2+}.

2. It has been established that the chief factor preventing coprecipitation of copper under the conditions used is complex formation.

3. It has been shown that in the series: ammonium hydroxide – glycine – ethylenediamine, the capacity for preventing coprecipitation of copper increases from left to right, i.e., with increasing stability of the respective copper complexes.

4. It has been established that at certain concentrations of glycine and ethylenediamine coprecipitation of copper during precipitation of hydrated ferric hydroxide by ammonium hydroxide in the cold is practically nil (for the concentrations of Fe^{3+} and Cu^{2+} used).

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1) See Consultants Bureau Translation, page 177.
2) See Consultants Bureau Translation, page 303.

REMARKS ON A METHOD BASED ON FRACTIONAL CRYSTALLIZATION OF THE DOUBLE NITRATES OF MAGNESIUM AND THE RARE-EARTH ELEMENTS

G. Virts

One of the methods which has been recommended for a long time for the separation of mixtures of the rare earths of the cerium groups is fractional crystallization of the double magnesium nitrates of these elements. Crystallization of solutions of these salts is usually carried out by cooling hot solutions in the air without stirring, whereby a coarse crystalline film is formed. Sometimes, though rarely, stirring during cooling is recommended; in such cases a fine crystalline mass instead of a compact mass is formed [1].

Quantitative results which would permit a comparison of the efficiency of the different techniques of crystallization to be made are not available in the literature.

The results set forth in this paper, however, show that these purely methodological factors have considerable significance in deciding the efficiency of separation by fractional crystallization.

Appreciable differences in the efficiency of fractionation were observed when mixtures of cerium earths were subjected to fractional crystallization of the double magnesium nitrates, according to the method of crystallization employed. This observation was the reason we decided to carry out some experiments to find out the most favorable method of crystallization.

A mixture of cerium earths was used for these tests, of the metals contained, cerium was removed practically completely, while most of the lanthanum was separated and some of the praseodymium. The composition of this mixture was as follows: La 5%, Ce < 0.1%, Pr 6.5%, Sm 4.5%, Ga 3%, yttrium earths ca. 2%, the remainder Nd. A solution of the double magnesium nitrate salts of the components in this mixture was prepared in the usual way.

When this method of crystallizing the double magnesium nitrate salts is used, it is possible to divide the rare earths indicated above into two groups: the less soluble one containing the elements neodymium, praseodymium, and lanthanum (the group called the "didymium group" and denoted by the symbol Di) and the more soluble one, containing samarium and the elements which follow it (here called the "smarium group" and denoted by the symbol Sa). The large difference in the solubility of the double magnesium nitrate salts between neodymium and samarium is characteristic.

Radioactive europium was added to the nitrate solution for quantitative control of crystallization. Europium is a typical element of the samarium group and is suitable for tracing the distribution of this group among the various fractions.

After separation of the mother liquor from the crystalline mass, the rare earths contents of both fractions were determined. Further by counting the β-impulses on a Geiger-Muller counter, the content of radioactive europium was determined in aliquots of the oxides of both fractions. For denoting the result of fractionation, the coefficient of fractionation K was calculated by means of the formula:

$$K = \frac{\text{Amount of Di-oxides}}{\text{Amount of Sa-oxides}}$$ (in the crystals)

$$K = \frac{\text{Amount of Sa-oxides}}{\text{Amount of Di-oxides}}$$ (in the mother liquor)

For the determination of K according to the results available, i.e., from the rare earths content in the crystalline mass and the mother liquor used from the number of impulses/minute/mg of the oxides of both fractions, it was assumed on the basis of the composition given above that the amount of added radioactive europium represents ca. 10% of those rare earths in the original material which were designated as the samarium group. Although the assumption is not quite unarbitrary, nevertheless the errors to which it can give rise do not lead to appreciable distortions of the results given below.

In the first experiments (see Series A, Table 1), the original solution was evaporated and the hot solution cooled slowly in the air so that crystallization was spontaneous. It was found that spontaneous crystallization only proceeds in a regular manner for strongly supersaturated solutions. The values of K obtained thus are relatively low and vary considerably.

TABLE 1

Relationship between Fractionation Efficiency and Method of Crystallization

Expt. No.	Series	% Crystallization	Impulses/min/mg of oxide		K	Notes		
			In crystals	In mother liquor				
1	A	48.3	3.42	15.86	5.3			
3	A	67.3	5.45	18.16	3.9			
4	A	58.0	4.28	16.08	4.3			
5	A	63.7	6.18	16.79	3.1			
6	B	59.6	2.97	19.60	9.3			
8	B	61.8	3.93	19.85	6.1			
9	B	71.3	4.97	22.30	5.5			
						Cooling conditions °C		
						From	To	Minutes
10	C	61.1	2.45	21.20	10.7	74	25	31
13	C	64.2	2.95	21.95	12.7	89.5	23	55
11	C	64.2	1.95	23.75	15.6	88	22	95
12	C	63.6	2.06	21.90	13.6	91.5	25	300

Original material: 9.56 impulses/minute/mg oxide.

On an average, better, though still variable fractionation results were obtained by seeding the hot solutions, followed by slow cooling in air (see Series B, Table 1). Here, in contrast to the experiments of Series A, crystallization starts from the hot solution, but even in these cases supersaturation could be observed.

In the third series of experiments (see Series C, Table 1), a method which is rarely used in practice was adopted. The hot solution was seeded and then stirred vigorously with a mechanical stirrer, and then fairly rapidly cooled to room temperature with continued vigorous stirring. Small but well-formed crystals developed when this technique was employed. They were separated from

the mother liquor by squeezing them well and long on a Nutsch filter. When this method was adopted and the conditions were maintained constant the reproducibility was reasonably good. Crystallization rate has a marked effect on fractionation efficiency. Experiments, the results of which are given in the table, differ from each other in cooling rate.

Very rapid cooling gives poor fractionation probably because equilibrium cannot be fully established between the surface of the growing crystal and the solution. Under the conditions employed, however, even a one-and-a-half hour period of recrystallization gave maximum fractionation efficiency. Results of the fractionation obtained under the conditions of the 11th experiment can be regarded as very favorable.

The influence of the other factors was also studied while using the conditions of Series C. Thus it is interesting to know what values of K are obtained for varying degrees of recrystallization of the rare earths. In the experiments of Table 1, Series C, 61-64% of the rare earths was recrystallized. Some subsequent experiments with the same starting material were carried out under the same conditions as those employed in experiment No. 11. In these experiments, despite vigorous stirring there was initially some supersaturation; it became appreciable in the course of a few minutes for a relatively more complete crystallization, while the temperature of the solution increased by one or more degrees. The temperatures reached during this increase are indicated in the third column of Table 2. Determination of this temperature is a comparatively sensitive method of determining the extent of crystallization from the hot solution. The boiling point of the neutral salt solutions can also be used for this same purpose.

TABLE 2

Relationship between the Fractionation Coefficient and the Extent of Recrystallization of Rare Earths

Expt. No.	% Recrystallization	Temperature of crystallization °C	Impulses/min/mg oxide		K
			Crystals	Mother liquor	
17	43.3	57.3	1.40_3	15.0_0	12.5
14	51.2	66.5	1.46_0	16.8_2	13.9
19	64.5	75.7	1.91_3	21.7_0	14.5
18	65.4	78.1	1.89_5	22.1_5	15.1
15	74.1	86.0	3.09	25.9_2	11.4

Original material: 9.56 impulses/min/mg of oxide.

Experiment showed a small (hardly exceeding the experimental error) increase in the fractionation coefficient on increasing the amount of crystallized material; for an even greater degree of crystallization a fall in the fractionation coefficient occurs. In these experiments, of course, one cannot expect a constant value for K. A constant value can only be expected under isothermal crystallization conditions and when a thermodynamic equilibrium between the crystals and mother liquor exists. Moreover one of the components should be present in micro amounts [2].

If crystallization is carried further there should be an appreciable error, as a result of incomplete separation of crystals from mother liquor. This leads to a decrease in K. In addition, stirring the crystals and mother liquor towards the end of crystallization (at least as far as the conditions used in our experiments were concerned) becomes mechanically difficult. If it is desired to crystallize out more than two-thirds of the rare earths from a neutral solution, then particular attention must be paid to stirring during crystallization and to as full a separation as possible after crystallization.

The significance of the fractionation efficiency for fractions of different composition is of some interest for the application of this crystallization method. Table 3 contains results of some experiments carried out on fractions poor in the Sa group; i.e., fractions obtained from the crystals. It is possible to assess the composition of these fractions from the number of impulses/minute/mg of oxide, which is approximately proportional to the content of the Sa group of elements in the respective fraction. At the bottom of Table 3 are shown results for fractions rich in the Sa group. These experiments were also carried out under the conditions used in experiment No. 11 (Table 1). In calculating K the changing composition of the original solution with respect to the Sa group is taken into account.

TABLE 3

Relationship between the Fractionation Coefficient and the Content of the Samarium Group in the Original Solution

Expt. No.	Impulses/min/mg of original solution	% Crystallization	Impulses/min/mg		K
			Crystals	Mother liquor	
25	0.39_4	66.3	0.063	1.27_2	20.4
22	1.92	65.2	0.365	5.62	16.1
20	1.92	70.2	0.417	5.77	14.6
18	9.56	65.4	1.89_5	22.1_5	15.1
21	22.5	50.0	6.11	36.9	9.6
24	22.5	57.7	7.35	43.7	10.0
28	43.7	25.1	18.57	51.0_5	4.8

Results are somewhat better for fractions which are poor in Sa group elements, while the results are worse in cases where the fractions are richer in the Sa group. With regard to the latter it should be noted that the neutral solutions of the double magnesium nitrate salts rich in Sa crystallize out the poorer, the more the contaminants of the original material, such as iron, calcium and alkaline elements concentrate in the fractions rich in Sa.

These results show that fractional crystallization of the double magnesium nitrates is a suitable crystallization method for getting fractions rich in samarium and gadolinium from mixtures of cerite earths (ca. 10%) poor in these elements. A one-stage crystallization of two-thirds of the material is sufficient to decrease the content of the Sa group in a rare-earths mixture by five times.

Experiments described here with mixtures of cerite earths can be applied without any difficulty to rare-earth mixtures which are richer in lanthanum or containing cerium (III), since the double magnesium nitrates of these elements are slightly more sparingly soluble than those of neodymium.

SUMMARY

The effect of crystallization method on the efficiency of fractionation of mixtures of cerite earths, using fractional crystallization of double magnesium nitrates, has been investigated. Using radioactive europium, the separation of cerite earths into a less soluble fraction (Nd, Pr, La) and a more soluble fraction (Sm and the rare earths which follow it) was carried out almost quantitatively.

These methods of crystallization were: 1) spontaneous crystallization with slow cooling of the hot solution in air without stirring; 2) seeding the hot solution followed by slow cooling in air without stirring; 3) seeding the hot solution followed by cooling with vigorous stirring.

The third method gives the best fractionation. The second is better than the first.

When the third method is used, it is better to cool slowly than rapidly. When a large part of the rare earths is crystallized out (more than two-thirds in the crystallized fraction), fractionation is poor. Fractionation efficiency is better the lower the content of the Sa group elements in the cerite earths.

Fractional crystallization of the double magnesium nitrates by this method permits a rapid separation of Sa group elements from mixturesof cerite earths which are relatively poor in these elements.

Received May 13, 1954

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QUANTITATIVE DETERMINATION OF ALKYL-SUBSTITUTED 1-METHYL-4-PIPERIDONES

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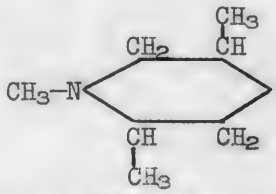
1,2,5-Trimethyl-4-piperidone —  — one of the alkyl-substituted γ-piperidones is of particular interest, since it is an intermediate in the synthesis of promedol, which is a new and effective anesthetic. Since, as far as we know from the literature, there is no method for the quantitative determination of 1,2,5-trimethyl-4-piperidone, we made the development of such a method our object. Since it is a base and at the same time has ketonic properties, 1,2,5-trimethyl-4-piperidone gives salts with acids and forms an oxime with hydroxylamine. We used these reactions for its quantitative determination. 1,2,5-Trimethyl-4-piperidone is easily titrated with both 0.1 and 0.5 N hydrochloric acid using bromocresol green (99.64%; 99.31%; 99.84%).

The correctness of our choice of indicator was confirmed by the fact that during potentiometric titrations the potential jump at the equivalence point corresponds with the color change of this indicator. Oxime formation also proceeds quantitatively under certain conditions.

We used a 5% hydroxylamine hydrochloride solution (for its preparation see below), which was added to our ketone after preliminary neutralization of the ketone with 0.5 N hydrochloric acid.

Oxime formation was carried out both in the cold and on heating for various periods. The hydrochloric acid formed during oxime formation was titrated with 0.5 N alkali to a color the same as that of a blank test.

Best results were obtained by heating at 80° for 2 hours. In the first experiments based on oxime formation, neutralization of 1,2,5-trimethyl-4-piperidone with hydrochloric acid was carried out (without indicator) using the same amount of 0.5 N hydrochloric acid as was used for titrating an equal aliquot of ketonic solution, but using bromocresol green.

In later experiments, in order to simplify the method we neutralized the same aliquot of ketone with 0.5 N hydrochloric acid, using bromocresol green as indicator, as was subsequently used for oxime formation. In this case exactly the same number of drops of bromocresol green was used for the blank as was used for the preliminary neutralization of the ketone.

When the hydrochloric acid which is liberated during oxime formation is titrated using bromophenol blue as indicator (when the ketone is neutralized by addition of the calculated amount of acid), there is a clear-cut color change at the equivalence point.

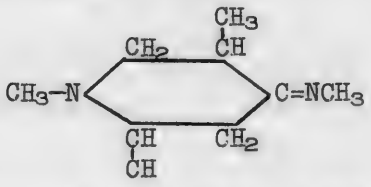
The substitution during this titration of bromophenol blue for bromocresol green when the ketone is neutralized beforehand to an indicator end point is

undesirable, since the color change is not so sharp. (The titration of the ketone itself with acid using bromophenol blue as indicator leads to a drawn-out color change). As a consequence, it is recommended that the hydrochloric acid should be titrated during the oxime reaction in the presence of two indicators: the results obtained are the same as with bromophenol blue alone.

E.g., 99.56%, 99.69%, 99.25% (for preliminary neutralization of ketone using the calculated amount of acid; titration of the hydrochloric acid formed during oxime formation was done in the presence of bromophenol blue).

99.29%, 99.19% (for preliminary neutralization of ketone using bromocresol green as indicator; the hydrochloric acid formed during oxime formation was titrated using bromocresol blue).

These methods were developed using 1,2,5-trimethyl-4-piperidone which had been purified by conversion through the hydrochloride, and by distillation. The material boiled at 70-72° under 8 mm vacuum. Technical 1,2,5-trimethyl-4-piperidone, depending on how it is made, can contain: neutral ketones (allyl-isopropyl ketone and the methoxy derivatives corresponding to it), and also 1,2,5-trimethyl-4-methyliminopiperidine.



1,2,5-Trimethyl-4-methylimini o piperidine was shown experimentally to titrate quantitatively with acid. It requires, however, two equivalents of acid and not one, since on hydrolysis it forms methylamine and 1,2,5-trimethyl-4-piperidone. The 1,2,5-trimethyl-4-piperidone thus formed undergoes the oxime reaction under the conditions indicated above. If, therefore, the above mentioned products are present in technical 1,2,5-trimethyl-4-piperidone, the latter is determined as follows:

An aliquot of the technical product is first titrated with acid using bromocresol green as indicator, the neutralized ketone is subsequently extracted with ether, while the residue after ether extraction is treated with hydroxylamine under the same conditions as used for pure 1,2,5-trimethyl-4-piperidone. The excess (mls) of hydrochloric acid used for preliminary neutralization of the technical product minus the amount (mls) of alkali used for neutralizing the hydrochloric acid liberated during oxime formation, multiplied by two, is equivalent to the amount of 1,2,5-trimethyl-4-methylimin o piperidine.

1,2,5-Trimethyl-4-piperidone is determined from the difference between the doubled amount (mls) of alkali used after oxime formation and the amount (mls) of hydrochloric acid used for neutralizing the aliquot.

Thus in a synthetic mixture consisting of 19.2% neutral ketones, 9.4% of 1,2,5-trimethyl-4-methyliminopiperidine, and 71.4% 1,2,5-trimethyl-4-piperidone, 70.2% of the latter and 9.5% of 1,2,5-trimethyl-4-methyliminopiperidine were found. This is quite a satisfactory result for a technical product.

On the assumption that the method developed for 1,2,5-trimethyl-4-piperidone is applicable to other alkyl-substituted 1-methyl-4-piperidones, we tried it out on 1,2,5-trimethyl-6-ethyl-4-piperidone[1] (b.p.. at 3 mm 77-79°) and got good results (see Table).

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[1] The 1,2,5-trimethyl-6-ethyl-4-piperidone, as well as the 1,2,5-trimethyl-4-methyliminopiperidine, were kindly given to us by V. A. Rudenko of the Institute of Organic Chemistry, Acad. Sci. USSR, for which we wish to thank him.

TABLE

Wt. of material, in g	Vol. of 0.5 N HCl used, in ml	Amount of 1,2,5-trimethyl-6-ethyl-4-piperidone (by titration with HCl) in %	Amount of 0.5 N NaOH used, in ml	Amount of 1,2,5-trimethyl-6-ethyl-4-piperidone (by oxime formation with 5% hydroxylamine) in %
0.5253	6.16	99.24	6.15	99.08
0.5371	6.31	99.42	6.32	99.58
0.5524	6.47	99.12	6.50	99.58
0.5562	6.53	99.35	6.55	99.66

EXPERIMENTAL PROCEDURE

a) 0.5-0.6 g of the pure preparation (exact weight) is measured out with a Lunge pipet into a 100 ml conical flask, 2 drops of bromocresol green are then added, and the solution titrated with 0.5 N hydrochloric acid to a yellow color. 25 ml of 5% hydroxylamine hydrochloride solution is then added, and the mixture heated under reflux at 80° for 2 hours on a water bath. The hydrochloric acid evolved is titrated with 0.5 N sodium hydroxide to a color equal to that of a blank carried out in parallel, containing exactly the same amount of hydroxylamine hydrochloride, indicator, water, acid and alkali as used for the sample itself.

b) 0.6-0.7 g of the technical product (exact weight) is measured out with a Lunge pipet into a 50 ml separating funnel, 2 drops of bromocresol green are added and the solution titrated with 0.5 N hydrochloric acid to a yellow color of the solution. The solution is then extracted twice with ether (in 15 ml lots). The aqueous solution is run off into a 100 ml conical flask, the ether solution is washed twice with water in 5 ml lots, and the wash water added to the total aqueous extract. Subsequent procedure is the same as for the pure compound.

The percentage content of 1-methyl-4-piperidone is calculated from the formula:

$$\frac{(2b - a)\cdot M\cdot 100}{2\cdot 1000\cdot K} = \% \text{ content},$$

where b is the amount of 0.5 N sodium hydroxide used for titrating the acid after oxime formation (in mls); a is the amount of 0.5 N hydrochloric acid used for titrating the aliquot (in mls); M – the molecular weight of the substituted γ-piperidone; K – weight of aliquot, in g.

The percentage content of alkyl-substituted 1-methyl-4-methyliminopiperidine is calculated from the formula:

$$\frac{(a - b)\cdot 2\cdot M\cdot 100}{2\cdot 1000\cdot K} = \% \text{ content}$$

The legends are the same as above.

Preparation of 5% Hydroxylamine Hydrochloride. 50 g of hydroxylamine hydrochloride is dissolved in 90 ml of water at 80-90° (if the solution is turbid, it should be filtered). 300 ml of alcohol and 6 ml of bromophenol blue indicator are added. The solution is neutralized with alcoholic alkali to a bottle-green color, when it is made up to a liter with alcohol.

Preparation of Bromophenol Blue Solution. 0.4 g of indicator is dissolved in 10 ml of 0.1 N sodium hydroxide and diluted with water to 100 ml.

SUMMARY

1. Methods are described for the quantitative determination of pure alkyl-substituted 1-methyl-4-piperidones: a) by titration with hydrochloric acid using bromocresol green as indicator; b) by oxime formation after neutralization with hydrochloric acid.

2. A method is given for the quantitative determination of alkyl-substituted 1-methyl-4-piperidones and alkyl-substituted 1-methyl-4-methyliminopiperidines in the technical product.

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[1)] See Consultants Bureau Translation, page 683.

COLOR REACTION OF COMPLEX FORMATION BETWEEN ELEOSTEARIC ACID AND PICRIC ACID AS A QUALITATIVE TEST FOR TUNG OIL

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The capacity of highly nitrated organic compounds to react in virtue of their non-valency forces with multiple carbon bonds has been known for a long time [1,2]. A characteristic example of such a reaction is that of tetranitromethane to give colored complexes with almost all carbon compounds having multiple bonds.

Of special interest from this point of view is picric acid which, thanks to its capacity of forming complexes with aromatic compounds, has found wide application for the identification of the latter [1]. These reactions of picric acid are very often color reactions and in individual cases have been used as color tests [3,4].

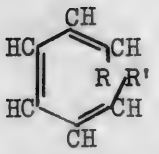
Picric acid can only form complexes with aromatic hydrocarbons, and amines and their derivatives. The only exception is pinene picrate. A method of separating aromatic hydrocarbons from other compounds is based on this fact [1,2].

Results are often given in the literature of color reactions of picric acid with other compounds containing ketonic and aldehyde groups, carbohydrates, glucosides, etc., which, however, do not belong to the aromatics but are more often representative of aliphatic or hydroaromatic compounds. It should be noted that all these color reactions [5,6,7] are carried out between the types of compounds just mentioned and picric acid in a solution of the alkali salts of the latter. In so far as is known the picric acid itself in alkaline media gives colored compounds of the nitron acid type [2]; all the color reactions are not really the result of direct interaction between picric acid and test material, but are simply an intensification of the color reaction between alkali and picric acid. In view of the instability of these intensification processes, their application as colorimetric methods is restricted. In order to avoid such difficulties during a study of the reaction between picric acid and the compounds we were interested in, the reactions were all carried out in acid or neutral media.

In studying the properties of eleostearic acid, we reckoned that picric acid, just like other nitro compounds, should, under certain conditions, react to varying degrees to form complex compounds not only with the multiple bonds of aromatic hydrocarbons, but also with screened multiple bonds and with any carbon multiple bond.

This is more than probable in the case of eleostearic acid, since in certain cases the conjugated double bonds of this acid in solution may not only be stretched out in a zig-zag fashion along a straight line, but may be twisted into a spiral [8].

This twisted arrangement of the carbon atoms in the molecule of eleostearic acid with conjugated double bonds can be represented as follows:



$R = -(CH_2)_3CH_3$

$R' = -(CH_2)_7COOH$

In some cases 6 of the carbon atoms of eleostearic acid with conjugated double bonds may have a spatial configuration — not related, of course, to their other configurations — and, consequently be in a general electrodynamic state [9,10] very similar to that in such aromatic compounds as give picrates. This fact is probably one of the major reasons for a non-valency interaction between picric acid and eleostearic acid.

We found that like many other compounds, picric acid in solution in acetic acid, ether, acetone, dichloroethane, etc., reacts even at room temperature with eleostearic acid — an aliphatic compound. This is confirmed by the appearance of a garnet -red color.

Experiments on intensifying this reaction by adding anhydrous salts to the reaction media: sodium and mercuric acetate, and also anhydrous cupric and ferric sulfates, did not give positive results.

It was subsequently shown that a similar color reaction also occurs when picric acid reacts with an acetic acid solution of eleostearic acid in the initial stages of polymerization. It was also observed when eleostearic acid was fused with picric acid, and on melting eleostearic acid in hot saturated aqueous solutions of picric acid. A rather curious phenomenon was observed in this case, viz., a change in color of the picrates formed. On removal of the solvents listed above, or on cooling the fused picrates to room temperature, their color changed from a garnet-red to a light yellow; they regained their garnet-red color on dissolving them in the same solvents or on heating them. Thus both the solvents we used as well as heat can intensify the color.

Eleostearic acid was isolated from the picrates formed by treating the latter with aqueous ammonia. This led us to conclude that these picrates are molecular compounds of a complex type.

Analyses of these complexes showed that in contrast to the aromatic hydrocarbons which form complexes with picric acid in the ratio 1:1, eleostearic acid complexes with picric acid in the ratios 10:1, 5:1, and 3:5. The melting points of these complexes are not sharp and vary within the limits 68-70°.

It was shown experimentally that the changes in color intensity of the compounds formed between picric acid and eleostearic acid do not follow Beer's law, and that the sensitivity of a method based on this reaction is 91 mg/2 ml.

We did not use this reaction therefore for colorimetric determination of eleostearic acid. This reaction however can be used under certain conditions as a qualitative test for this acid.

Picrates of aliphatic compounds (apart from various amines) have not hitherto been described, nor a color reaction between picric acid and aliphatic compounds. This reaction of eleostearic acid with picric acid, therefore, can be regarded as the first example thus far described of a reaction between picric acid and an aliphatic compound, and also the first instance of a color reaction between picric acid and an aliphatic compound.

Tung oil, which sometimes contains 80% eleostearic acid, is completely analogous in behavior to eleostearic acid with respect to its reaction with picric acid. This is very interesting from a practical point of view, since in general there is no color test known for tung oil. The two qualitative but non-color

reactions for tung oil are based on [11, 12] it capacity to gelatinize on simple heating, or according to Marcuson, on the reaction of its ether solution with ferric chloride. These reactions, however, cannot be used for detecting tung oil in the presence of other oils if there is less than 10% of tung oil present in the mixture [13]. It is possible to work out a colorimetric method for tung oil in admixture with other oils by using a reaction discovered in 1919, viz., diazotization of diene hydrocarbons [14]. This reaction was successfully used by A. P. Terentyev both as a qualitative test for diene hydrocarbons with conjugated double bonds [15, 16], and for the qualitative detection of eleostearic acid in tung oil [17].

We have worked out a colorimetric method by means of which tung oil can be determined in the presence of other plant and animal oils when the tung oil content is not less than 1%. The existing method [3] of detecting mineral oils in plant oils, which is based on adding a benzene solution of picric acid to the test material, is not specific for mineral oils since the possible presence of tung oil in the mixture is overlooked.

EXPERIMENTAL

1. Preparation of Starting Materials.

a) Eleostearic Acid. 100.0 g of tung oil was dissolved in 300.0 ml of 10% alcoholic NaOH and the mixture heated on a water bath under reflux for 6.5 hours. While still hot, the thick transparent mass was transferred to a beaker and 1 liter of water and 400 g NaCl added. The soap layer on the surface was worked up a few times with saturated aqueous NaCl. The soap obtained was dissolved in the smallest possible amount of alcohol by heating. This solution while still warm was neutralized with 10% H_2SO_4 to a weak acid reaction (litmus). The mixture of fatty acids which separated out on the surface was an oily layer, which on cooling formed a solid mass which was removed from the aqueous solution. The mass obtained, which had the specific tung oil odor, was treated with water a few times until it gave a neutral reaction to litmus. The mass was then crystallized a few times from dilute aqueous alcohol according to the current method [13], the solution being cooled in an ice-salt mixture. After suction filtration on a filter funnel the eleostearic acid had a melting point of 61-63°.

In order to convert the α-isomer into the β-isomer, this mass of crystals was dissolved in 400 ml of 60% alcohol and boiled under reflux for 6 hours. After cooling it was recrystallized in the cold using an ice-salt mixture for cooling. The crystals after suction filtration had a melting point of 69-70.5° and after repeated crystallization, 71-72°.

b) An aqueous solution of picric acid saturated with the latter at 70° was prepared by heating excess picric acid with water at 80° and filtering the hot solution at 70°.

c) An aqueous solution of picric acid saturated with the latter at room temperature (18°) was prepared by cooling solution (b) to room temperature and filtering the cooled solution.

d) A saturated solution of picric acid in acetic acid was made by cooling a boiling saturated solution of picric acid in acetic acid to room temperature and filtering.

2. Color Reaction of Eleostearic Acid and a Color Test for Tung Oil

2.0 ml lots of acetic acid saturated with picric acid at room temperature were placed in 3 test tubes. 0.2 g of eleostearic acid was added to the first, an equal amount of eleostearic acid in its initial polymerization stages to the second, and 5 drops of tung oil to the third.

After shaking tubes and contents for 1/2 minute at room temperature, the mixtures in all three test tubes acquired an intense garnet-red color.

Similar color changes occurred when, instead of the acetic acid solution saturated with picric acid at room temperature, saturated solutions at room temperature of picric acid in acetone, ether, benzene, butanol and dichloroethane were used.

The sensitivity is 91 mg/2 ml.

3. A Color Test for Tung Oil in the Presence of Other Oils.

Test solutions of 1,2,5, and 10% of tung oil in sunflower oil were made. Similar solutions of tung oil in soya and linseed oils respectively were also made; 12 solutions in all.

15 drops of these 12 samples were placed in test tubes and 2.0 ml of acetic acid saturated with picric acid at room temperature added to each.

The controls were test tubes containing pure sunflower, soya and linseed oils, respectively, to which the same amount of the picric acid-acetic acid solution had been added.

The following changes were observed after shaking the test tubes for 2-3 minutes at room temperature. After 30 minutes a layer of oil floated on the surface of the glacial acetic acid. A weak orange color could be detected in the oil layer for a 1% concentration of tung oil. This color was stronger when 2% was present in the oily layer floating on the surface; no color change was observed in the oil layer in the control tests.

4. Complex Compounds of Eleostearic Acid with Picric Acid

a) 250 ml of water saturated with picric acid at 70° was placed in a beaker and 5.0 g of eleostearic acid added (m.p . 71-72°). The beaker was placed on a boiling water bath and the mixture mixed thoroughly, the temperature was allowed to reach 80°; when the beaker was removed from the bath, an oily mass of a garnet-red color formed on the surface of the solution. The mixture was stirred until the temperature reached 60°, when it was allowed to cool to room temperature. The red oily liquid floating on the surface changed into a light yellow solid mass on cooling. This was separated from the liquid with a porcelain spatula and placed in a porcelain mortar. The mass was carefully triturated 2-3 times with water saturated with picric acid at room temperature, ca. 20 ml of solution being used each time.

The triturated mass was washed with 20 ml of the same aqueous picric acid solution and then with 50 ml distilled water. The washed precipitate was finally dried between sheets of filter paper and in a desiccator over $CaCl_2$.

The light yellow product obtained turned garnet-red in color on fusing but regained the light yellow color on cooling; m.pt. 68-70°.

Found %:	C 74.34, 74.29;	H 10.03, 10.27;	N 1.30, 1.45
Calculated %:	C 74.13;	H 10.13;	N 1.39

$$(C_{18}H_{30}O_2)_{10}[(NO_2)_3C_6H_2OH] = C_{186}H_{303}O_{27}N_3$$

b) 13.5 g of eleostearic acid and 9.0 g of picric acid were placed in a test tube which was then immersed in a water bath to the level of the reaction mass inside the tube. On heating to 70-90° the whole melted and changed into a garnet-red liquid. The liquid was maintained at this temperature for 10 minutes and stirred with a thermometer. The liquid was then allowed to stand at 90° for 3 minutes without stirring. The test tube was removed from the bath and allowed to cool to room temperature. When this was done, the formation of two separate layers was observed, the upper one a transparent red layer and the lower an opaque red layer. On cooling to room temperature the color of both layers changed from a yellowish-red to a pale yellow. The test tube was carefully cut at the junction of the two layers and the two parts separated.

The m.p. of both layers was 68-70.5°.

The lower layer analyzed as follows:

Found %: C 50.01, 50.55, 51.14; H 5.46, 5.54, 5.52; N 10.54, 10.58
Calculated %: C 50.94; H 5.34; N 10.61.

$(C_{18}H_{30}O_2)_3[(NO_2)_3C_6H_2OH]_5 = C_{96}H_{105}O_{41}N_{15}$

While the analysis for the upper part was:

Found %: C 71.25, 71.34; H 9.75, 9.57; N 2.47, 2.70
Calculated %: C 71.12; H 9.51; N 2.59

$(C_{18}H_{30}O_2)_5[(NO_2)_3C_6H_2OH] = C_{96}H_{153}O_{17}N_3$

A small amount of the two layers and some pure eleostearic acid, respectively, ground to a fine powder were spread in fine layers on watch glasses and allowed to stand in air at room temperature. After 3 days the eleostearic acid had polymerized, while the others remained in their powder form (to the hand).

5. Decomposition of the Complexes and Isolation of Eleostearic Acid

0.5 g of the material described in section (a) of 4 was heated at 50° to dissolve it in 150 ml concentrated ammonia. The solution was diluted with an equal volume of water and neutralized with 10% H_2SO_4 to a weak acid reaction. The solid mass which separated out was filtered off and washed with cold water until the wash water was no longer colored yellow. The precipitate was then passed through the same sequence of operations again.

The precipitate obtained after repeated crystallization from methanol and ether formed flat crystals with a m.p. of 69-71°. These crystals did not depress the m.p. of eleostearic acid, the mixed m.p. was 69-72°.

Similar results were obtained when both upper and lower layers from 4(b) were given the same treatment.

SUMMARY

1. Eleostearic acid gives a color reaction with picric acid.

2. A method has been worked out for the colorimetric detection of eleostearic acid and color tests for tung oil, both on its own and mixed with other oils developed. 1% tung oil can be detected in the presence of other oils.

3. Complex molecular compounds of eleostearic acid of the following composition have been isolated:

$(C_{18}H_{30}O_2)_{10}[(NO_2)_3C_6H_2OH]$; $(C_{18}H_{30}O_2)_5[(NC_2)_3C_6H_2OH]$;
$(C_{18}H_{30}O_2)_3[(NO_2)_3C_6H_2OH]_5$.

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CRITICISM

B. P. Nadeinsky. "Introduction to Analytical Chemistry," Moscow, Soviet Science, 1953, 364 pp. Printing 10,000. Price, 7 rubles 70 kopeks.

Soviet literature on analytical chemistry has been enriched by B. P. Nadeinsky's interesting book. As indicated in the foreword of the book, the theoretical foundations and calculations of analytical chemistry are considered. Textbooks which have been devoted exclusively to the theoretical questions of qualitative analysis have been in existence for a long time.

The book has a short introduction on the role of analytical chemistry and analytical methods: the book is divided into 11 chapters, in which the most important theoretical questions are discussed. At the beginning the author gives a brief review of the development of analytical chemistry in Russia, and also gives a short list of papers at the end of the chapter (only Soviet authors). This is useful to the reader, particularly students who want to know something about some of the outstanding achievements of Russian analysts and about the development of the theory and of new methods in analytical chemistry.

The second chapter, "Analytical Classification of Cations and the D. I. Mendeleev Periodic System," in contrast to those in many other textbooks, makes it quite clear that the division of cations into groups is not artificial, but is intimately connected with the periodic law.

In succeeding chapters chemical equilibria in analytical reactions, methods of expressing solution concentrations, and calculations of the concentration and activities of protons in solution are discussed. Separate chapters are devoted to hydrolytic processes, equilibria between solutions and precipitates, and also to oxidation-reduction reactions, complex compounds, and colloids in analytical chemistry. The book ends with a useful chapter on the sensitivity and specificity of analytical reactions.

In comparison with other books the material on buffer mixtures, equilibria between two precipitates in solution, and theory of precipitation by hydrogen sulfide is set out better; many good examples are adduced in dealing with these questions and with some others.

It is peculiar, therefore, that the most important question of the degree of electrolytic dissociation, on which all this depends, is not discussed; the solubility of sparingly soluble electrolytes is discussed in a niggardly fashion. It is not made clear on what factors the rate of chemical reactions is dependent, nor is anything said about ion solvation, and there is no clear explanation why strong electrolytes dissociate completely into ions. The subject of systems in equilibrium is barely touched upon, and no mathematical expression of the law of mass action is given. Unfortunately, throughout the whole book, in discussing analytical reactions, there is no indication that the reaction tends to follow the path whereby material with a lower concentration of ions in solution is formed.

We think that the title, "Introduction to Analytical Chemistry," does not define exactly the material set forth in this book. In effect the author has only considered the theoretical basis and related calculations.

The book is replete with numerous examples and problems which are treated in detail. Many of them are very important and are of very decided interest. True, Nadeinsky seems to be attracted more to solving these problems and is apt to forget to expound the principles on which they are based. Some chapters, particularly 5 and 6, are overloaded with examples which do not have any

direct bearing on the questions of qualitative analysis under discussion, but tend to obscure the chemical meaning of the processes and do not support the theoretical positions of the book. This is true, e.g., of the determination of the ionic composition of solutions of tri-basic acids (see p. 135). As an example of overloading the book with solutions of various problems, we may quote the excessive number of examples and detailed calculations of the molality of solutions which are rarely used (see pp. 82, 83, etc.). The activity of H^+ and OH^- ions in solutions of weak bases and acids is not clearly explained. These sections again are cluttered up with complex problems which are practically incomprehensible to students (see pp. 106-128). The number of problems could be reduced and their solutions simplified.

In general, there is quite a number of unfortunate or unnecessary choices of examples; e.g., No. 5, p. 64, the calculation on p. 170, example 6, p. 206, example 5, p. 236. No. 7, p. 228, cannot be solved if only the data available in the book are used. On the other hand, there are only a few examples on the important question of buffers in qualitative analysis.

The random nature in which the author has arranged his material is apparent in Chapter 6 on salt hydrolysis. The very concept of this important process and different instances of it are given only a brief treatment (see pp. 162-163). A large part of the chapter is devoted (pp. 165-200) to calculations of hydrolysis complicated by other processes. In addition, there is no information on such important practical examples as, say, the action of $(NH_4)_2S$ or Na_2CO_3 on Al^{3+} or Cr^{3+} ions. It would have been more expedient to explain the impossibility of forming, e.g., Al_2S_3 in aqueous solution; even in this case the author overlooks the chance of using simpler examples which are also of practical importance, in favor of examples which are not only more complicated but of little importance. For some unaccountable reason, formation of basic salts as a result of hydrolysis is not discussed in this chapter.

Chapter 9 on oxidation-reduction reactions was written in conjunction with G. E. Levant and is well written. It is a pity that the close relation between these processes and the Mendeleev periodic law is not shown. These reactions are not classified. In a review of the most important oxidizing agents, such important compounds as oxygen, MnO_2, concentrated sulfuric acid, and ferricyanide, have been omitted. A number of reducing agents has also been left out, and nothing is said about electric currents. While on p. 46, NO_2 is regarded as an oxidizing agent, on p. 287 this is correctly refuted. There it is emphasized that NO_2 possesses both oxidizing and reducing properties. It should have been explained how to change over from ionic equations to equations expressing reactions in molecular forms. There are no examples to explain oxidation-reduction reactions, e.g., solution of arsenic sulfide in nitric acid and reactions for complex and organic compounds.

The short chapter on colloids in analytical chemistry, which takes less than 9 pages, should be expanded. The position of colloid particles in dispersed systems should be demonstrated and their comparative sizes given. No emphasis is laid on an important fact in analytical chemistry — the formation of colloidal particles as an intermediate stage during all reactions involving preparation and solution of precipitates. Neither is anything said about "protective colloids," hydrophilic and hydrophobic, or about the significance of adsorption, which plays an important part in analytical chemistry. As against the usual custom, the author does not emphasize the importance of work carried out by Soviet scientists.

We should like to dwell here on an important methodological question, which from one point of view has not been solved satisfactorily in most textbooks. Should chemical equations be written with an equals sign or with an arrow?

Unfortunately the same author may, in the course of his own book, use both

conventions. B. P. Nadeinsky does this; e.g., the equation for the hydrolysis for ammonium acetate. On p. 164 this equation is written with an arrow while on p. 189 the identical equation is written with an equals sign. This is not a printer's error. It occurs over and over again and not only in Nadeinsky's book. There seems to be no logic about it at all. On p. 128 the electrolytic dissociation of sulfuric acid is written down as a two-stage process, the first stage with an equals sign and the second stage with the arrow sign. The number of such examples is countless.

How one should write chemical equations is not simply a matter of form. An equation should indicate the direction of a process and convey information. We are of the opinion that in general equals signs should not be used, since it senselessly equates reaction product with reactants. A chemical equation does not necessarily signify one reaction, and the reactants and reaction products cannot be dealt with like mathematical quantities. The weights of reactant and reaction products may be balanced, but at the same time important energy changes are taking place. Dropping the equals sign in no way destroys the validity of Lomonosov's law.

Substitution of an arrow for the equals sign immediately indicates the path of a reaction. The qualitative difference between materials found on the left and right-hand sides of a chemical equation follows from the very definition of the word "chemistry" itself. Two arrows $\rightleftharpoons$ should of course only be used for indicating completely reversible reactions. Nadeinsky is therefore wrong when he writes the electrolytic dissociation of water and tens of other reactions with two arrows of equal size.

For textbooks, particularly on analytical chemistry, the use of an arrow is of great methodological importance. In equations which represent reactions that go practically to completion (such reactions are the ones of greatest interest to analysts) one arrow alone should be used $\longrightarrow$. When reversible reactions occur, and it is desired to indicate the overall direction of the process, it is best to use two arrows differing in length $\rightleftharpoons$. Such a method explains the chemical meaning of a reaction more clearly.

The chapter on complex compounds is weak. The general bases concerning the composition and structure of these compounds are not pointed out and their great importance in analytical chemistry is not brought out convincingly enough. Some of the examples are unfortunate. On p. 45 it is written that excess reagent forms $Na[Ag(S_2O_3)]$ and $Na_2[Cu_2(S_2O_3)_2]$. This is not true; $Na_3[Ag(S_2O_3)_2]$ and $Na_3[Cu(S_2O_3)_2]$ are formed. The equations on p. 243 are for some reason printed in the reverse order. When cobalt and silver complexes of ammonia decompose in aqueous solution, ammonia is not formed, etc.

In a chapter on complex compounds, it would be desirable to give some information on coordination bonds, donors, and acceptors. Little is said about halogenoids and nothing about poly-acids, which are important in qualitative analysis. The author daringly affirms that "during complex formation, there is as a rule a sharp change of color" (see p. 242). There are numerous examples which do not confirm this.

The formation of $[Co(CN)_6]^{4-}$ (see p. 259) cannot be recommended as an example without a warning about the extreme instability of cobalticyanides. Otherwise the reader may get the impression that the method given by the author for the preparation of these ions is very simple.

The great drawback of the book is the absence of a theoretical treatment of physico-chemical analytical methods. In particular, there is no description of chromatographic methods, which are being used so successfully in analysis.

We should like to make some further special points. Chapter 5 has a large section on acid salts, but nothing about basic salts. In the section on indica-

tors, which is not so well written as the others, one would expect a modern definition of an indicator. In general, the theory of indicators is not considered.

There are errors in the description of precipitation of Group V cations (see p. 41). For many reasons the group's reagent should be used not on its own, but together with a small amount of ammonium salts, and in the presence of ammonia if insufficient ammonium salts are present.

It is stated on p. 225 that "the hydroxides of chromium and aluminum are more insoluble than their sulfides because the Cr^{3+} and Al^{3+} cations are precipitated as $Cr(OH)_3$ and $Al(OH)_3$." It is not a question of the lowest solubility but of the hydrolysis of the sulfides.

The author's statement (p. 70) re the equation $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ is not clear.

If the word dissociation is to be used, then it should be made clear what sort of dissociation is meant – thermal or electrolytic. Wouldn't it be better to say "ionization" instead of "electrolytic dissociation."

When the word soda is used it should be stated whether it is carbonate or bicarbonate. It is best to use chemical names.

In discussing Lomonosov's work in forming the first laboratory in Russia, reference should be made to his struggle with Shumakher and his pro-German reactionary group.

Among the portraits there is none of T. E. Lovits.

There is no subject index. The author repeats himself quite often, even on the same page.

There are a number of typographical errors.

All these drawbacks lower the value of the book.

We should like to see a new edition of this book free from all the drawbacks.

O. K. Dobrolyubsky.

May 8, 1954

Publishers note: Several paragraphs dealing with Russian grammar and spelling, violations of which in the book being reviewed are noted, have been omitted from this translation.

NEW REAGENTS

The All-Union Research Institute on Chemical Reagents wishes to inform all organizations and universities occupied with the application and testing of organic reagents for cations that the Institute has synthesized a new, highly sensitive organic reagent for the colorimetric determination of beryllium – "BERILLON II IREA."

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